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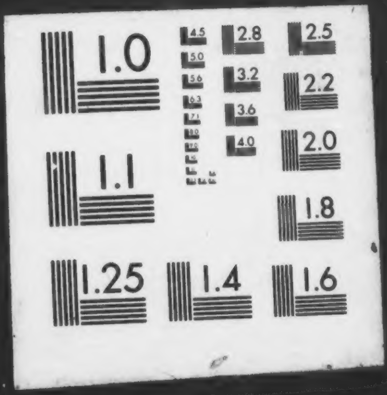
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# EPA/IERL-RTP Interim Procedures for Level 2 Sampling and Analysis of Organic Materials

Arthur D. Little, Inc., Cambridge, Mass.

**Prepared for**

Industrial Environmental Research Lab, Research Triangle Park, N C

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Laboratory
Research Triangle Park, North Carolina 27711

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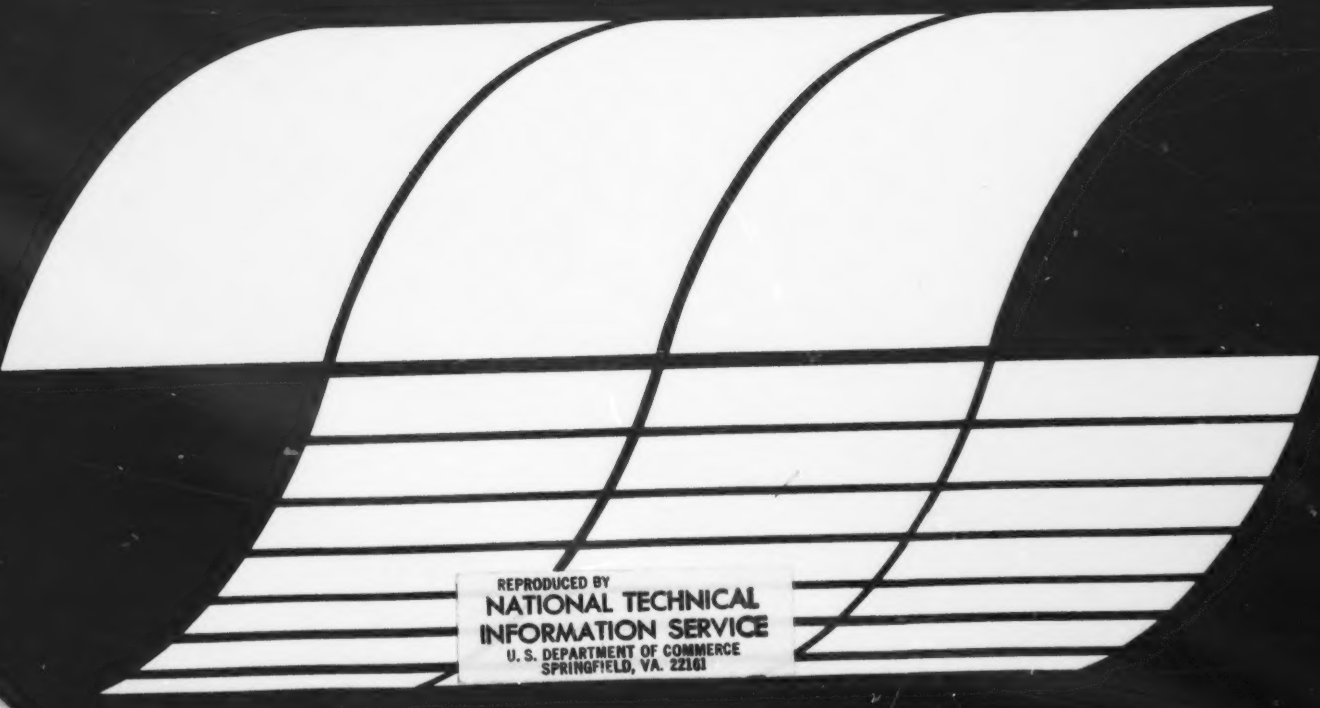
February 1978

# EPA/IERL-RTP INTERIM PROCEDURES FOR LEVEL 2 SAMPLING AND ANALYSIS OF ORGANIC MATERIALS

Interagency
Energy-Environment
Research and Development
Program Report



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16. ABSTRACT The interim report presents concepts and guidelines to be used in considering Level 2 sampling and analysis for organic compounds. It suggests specific procedures. (The final Level 2 organics procedures manual will include more fully developed concepts and procedures, specified as much as is possible for a wide range of conditions.) The report is intended for experienced research teams, thoroughly familiar with environmental sampling and analysis, Level 1 procedures, and the phased approach. It does not attempt to teach the detail which is more adequately found in other publications, but relies heavily on reports published previously by IERL-RTP and its contractors.

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by

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Contract No. 68-02-2150, T.D. 21102
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## TABLE OF CONTENTS

List of Tables . . . . . . . . . . . . . . . . . . . . . v

List of Figures . . . . . . . . . . . . . . . . . . . . vi

Foreword . . . . . . . . . . . . . . . . . . . . . . . vii

I. INTRODUCTION . . . . . . . . . . . . . . . . . . . . 1

A. Philosophy of the Phased Approach . . . . . . . 1

B. Purpose of a Level 2 Study . . . . . . . . . . . 2

C. Purpose and Scope of This Document . . . . . . . 3

II. LEVEL 1 TO LEVEL 2 TRANSITION . . . . . . . . . . . . 5

III. LEVEL 2 SAMPLING AND ANALYSIS: TENTATIVE PROCEDURES . 9

A. Sample Types and Sampling Methods . . . . . . . 9

B. Analysis Methods . . . . . . . . . . . . . . . . 11

1. Compounds in Predetermined Categories . . . 11

2. Unknown Samples . . . . . . . . . . . . . . . 18

IV. SAMPLING METHODS . . . . . . . . . . . . . . . . . . 25

A. Gases and Vapors . . . . . . . . . . . . . . . . 27

1. Gases . . . . . . . . . . . . . . . . . . . . 27

2. Vapors . . . . . . . . . . . . . . . . . . . . 32

B. Particulates . . . . . . . . . . . . . . . . . . 34

C. Liquids/Slurries . . . . . . . . . . . . . . . . 36

D. Solids . . . . . . . . . . . . . . . . . . . . . 40

E. Fugitive Emissions . . . . . . . . . . . . . . . 41

F. Reactive Compounds . . . . . . . . . . . . . . . 44

V. ANALYSIS METHODS . . . . . . . . . . . . . . . . . . 47

A. Liquid Chromatography . . . . . . . . . . . . . 47

B. High Performance Liquid Chromatography (HPLC). . 51

Table of Contents (continued)

1. Detectors . . . . . . . . . . . . . . . . . . . 51

2. Gel Permeation Chromatography . . . . . . . 54

3. Reverse Phase HPLC . . . . . . . . . . . . . 56

4. Normal Phase HPLC . . . . . . . . . . . . . . 57

C. Thermal Gravimetric Analysis . . . . . . . . . . 58

D. Gas Chromatography (GC) . . . . . . . . . . . . . 59

1. Detectors . . . . . . . . . . . . . . . . . . . 59

2. Columns . . . . . . . . . . . . . . . . . . . 60

3. Gas Chromatographic Conditions . . . . . . 60

E. Gas Chromatography/Mass Spectrometry . . . . . 62

1. Detector . . . . . . . . . . . . . . . . . . . 62

2. Columns . . . . . . . . . . . . . . . . . . . 65

F. Mass Spectrometry (LRMS and HRMS) . . . . . . . 65

1. Low Resolution Mass Spectrometry . . . . . 65

2. High Resolution Mass Spectrometry . . . . . 66

G. Infrared Spectroscopy (R) . . . . . . . . . . . 68

H. Nuclear Magnetic Resonance Spectroscopy . . . . 69

I. Ultraviolet and Luminescence Spectroscopy . . . 71

APPENDIX A. Expected Distribution of MEG Category Organic Compounds in Level 1 Samples . . . . . . . . . 73

APPENDIX B. Bibliography . . . . . . . . . . . . . . . . . . 101

# List of Tables

| Table Number | | Page |
|---|---|---|
| 1 | Comparison of Level 1 Data with Decision Criteria | 6 |
| 2 | Level 2 Preferred Sampling and Sample Treatment Methods for Various Organic Chemical Categories | 13 |
| 3 | Level 2 Analysis Methods by MEG Category | 16 |
| 4 | Problematic Organic Compound Categories | 45 |
| 5 | Comparative Specifications of HPLC Detectors | 52 |
| 6 | Electronic Absorption Bands for Representative Chromophores | 53 |

## LIST OF FIGURES

| Figure Number | | Page |
|---|---|---|
| 1.a. | Level 2 Organic Analysis Scheme . . . . . . . | 20 |
| 1.b. | Organic Extracts Analysis Scheme . . . . . . | 21 |
| 2 | Integrated Gas Sampling Train . . . . . . . . | 28 |
| 3 | Porous Polymer Vapor Sampling Method . . . . | 30 |
| 4 | Porous Polymer and Thermal Gradient Sampling Train . . . . . . . . . . . . . . . | 31 |
| 5 | XAD-2 Sorbent Trap Module . . . . . . . . . . | 33 |
| 6 | Method 5 Train Modified for Collection of Organic Vapors . . . . . . . . . . . . . . | 35 |
| 7 | Source Assessment Sampling Schematic . . . . | 37 |
| 8 | Method 5 Particulate Sampling Train . . . . . | 38 |
| 9 | Decision Example for "Worst Case" Site . . . | 43 |
| 10 | Directed Level 2 LC Scheme for Analysis of Phenols (MEG Category 18) . . . . . . . . . | 48 |
| 11 | Directed Level 2 LC Scheme for Analysis of Polychlorinated Biphenyls . . . . . . . . . | 49 |
| 12 | Directed Level 2 LC Scheme for Analysis of Polynuclear Aromatic Hydrocarbons . . . . . | 50 |
| 13 | Guide to Selection of HPLC Analytical Procedures . . . . . . . . . . . . . . . . . | 55 |

# FOREWORD

This document constitutes an interim guide to field and laboratory procedures for sampling and analysis of industrial effluent and process streams. The procedures are limited to those that will permit chemical analysis of organic species in these streams. They are intended to provide compositional data appropriate to Level 2 in the Phased Approach to Environmental Assessment. Since experience in this type of investigation is still rather limited. the present document is subject to further refinement and expansion before it can be considered complete. Additional data, including validated sampling and analysis procedures consistent with the objectives of Level 2 Studies will be developed for incorporation into the final version of this manual which is scheduled for completion later this year.

# I. INTRODUCTION

This Interim Procedures Manual represents a step in the development of a final Level 2 Procedures Manual for the sampling and analysis of organic compounds from process streams. Concepts and general guidelines are presented here. The final manual will contain the fully developed concepts and, insofar as possible, validated Level 2 procedures.

## A. Philosophy of the Phased Approach

The original philosophy used in the development of a phased approach to environmental assessment is briefly reviewed to place the purpose of a Level 2 study in context with the overall program. (1)

The Process Measurements Branch of IERL/RTP has developed a three-tiered or phased approach to performing an environmental source assessment. In this phased approach, three distinctly different sampling and analytical activities are envisioned. (2)

The phased sampling and analytical strategy was developed to focus available resources (both manpower and dollars) on emissions that have a high potential for causing measurable health or ecological effects, and to provide comprehensive chemical and biological information on all sources of industrial emissions.

The phased approach requires three separate levels of sampling and analytical effort. The first, Level 1, is designed to provide enough information about the composition of effluent and process streams to permit them to be ranked in order of priority for probable environmental hazard. The Level 1 assessment is intended to: 1) provide preliminary environmental assessment data, 2) identify principal problem areas, and 3) provide the data needed for prioritization of energy and industrial processes, streams within a process, components within a stream, and classes of materials, for further consideration in the overall assessment. The second phase of sampling and analysis effort, Level 2, is designed to provide additional information that will confirm and expand the information gathered in Level 1. This information will be used to define control technology needs and may, in some cases, give the probable or exact cause of a given problem. The third phase, Level 3, makes use of sampling and analysis methods whose precision and accuracy are sufficient to permit quantitative monitoring of specific pollutants identified in Level 2. Concentrations of critical components in a stream can thus be determined as a function of time and process variation with accuracy and precision necessary for effective control device development.

The phased approach offers potential benefits in terms of the quality of information that is obtained for a given level of effort and in terms of the costs per unit of information. This approach has been investigated and compared to the more traditional approaches and has been found to offer the possibility of substantial savings in both time and funds required for assessment.

The three sampling and analysis levels are closely linked in the overall environmental assessment effort. Level 1 identifies the questions that must be answered by Level 2, and Level 3 monitors the problems identified in Level 2 to provide information for control device design and development.

## B. Purpose of a Level 2 Study

The objective of a Level 2 Study will be to obtain more detailed and accurate data about the composition of a particular process stream than is available in the context of a Level 1 Study. The improved accuracy could either be primarily quantitative in terms of establishing a truly representative emission rate, or be primarily qualitative in terms of determining specific chemical composition or both. It is expected that most Level 2 sampling and analysis studies for organic compounds will be required to identify all of the specific chemical species present and detectable in process streams.

Most Level 2 studies will be probably done as a result of interpretation of data obtained from previous Level 1 studies. Level 2 inquiries are expected to be directed primarily at the identification, quantification and confirmation of specific compounds whose presence could be inferred on the basis of the categorical analysis of Level 1. For these cases, a restricted set of specified procedures may be selected. Level 2 studies may also occasionally be initiated either on the basis of results of the bio-tests alone or on other criteria than the Level 1 chemical analysis. Thus, the questions to be answered by Level 2 procedures may range from highly specific, (i.e. what is the amount and composition of polychlorinated biphenyls in the stream?) to quite general, (i.e. what caused the positive bio-test result?). In this latter example where Level 1 chemical analysis was apparently not sufficiently sensitive to reveal the existence of a hazardous composition, a comprehensive analytical effort similar to but more exhaustive than that required for Level 1 would have to be conducted, perhaps including detailed chemical analyses more characteristic of Level 2.

## C. Purpose and Scope of This Document

The objective of this document is to present concepts and guidelines to be used in consideration of Level 2 sampling and analysis for organic compounds. This interim report focuses on concepts and general guidelines, with suggestions for specific procedures. A definite Level 2 Organics Procedures Manual will eventually be published which will include the more fully developed concepts and procedures specified as much as is possible for a wide range of conditions.

The Level 2 Organic Procedures Manual is intended for use by experienced research chemists who are presumed to be thoroughly familiar with environmental sampling and analysis, with Level 1 procedures and with the objectives of the phased approach. The manual will not attempt to teach the detail which is more adequately found in other publications, but will rely heavily on reports published previously by IERL-RTP and its contractors (1-8). A reader who is not familiar with these documents should consult them before attempting to use the procedures described in the Level 2 organic sampling and analysis manual.

In addition, various standard methods such as published by ASTM, EPA (Federal Register), NIOSH and the Intersociety Committee are relied upon where appropriate.

The Multimedia Environmental Goals (MEG) study sponsored by IERL-RTP has resulted in the generation of a list of categories of organic and inorganic compounds (the MEG lists) and associated concentration levels representing their toxicity in various media. (8) Examination of these categories shows that they include almost all major classes of organic compounds (with the exception of a very few such as pesticides), and that the MEG list therefore represents a convenient means of organizing a productive approach to organic analysis and reporting of the results of a Level 2 inquiry. The MEG list of organic compound categories has been used advantageously in this manual to provide a practical basis for interpreting data and for selecting Level 2 procedures. Inasmuch as the present document is by no means to be considered final or definitive in its coverage of Level 2 needs, however, the use of the MEG categories should be understood in the context of a reasonable approximation which can be helpful in developing a sound approach to a comprehensive environmental assessment process. It is emphasized that reference to the MEG list in this report is focused on the categories and not on the individual compounds. The MEG categories encompass most groups for which analysis will be needed while the compound list is quite restricted.

## II. LEVEL 1 TO LEVEL 2 TRANSITION

The current Level 1 analysis for organic species is expected to result in the description of a number of compound categories and their observed concentrations. Comparison of the measured concentration of each category with an appropriate decision criterion will then establish a basis for proceeding with and/or directing more detailed Level 2 studies. The appropriate decision criteria must be chosen with the concurrence of the Project Officer, bearing in mind the specific objectives of the study for which the Level 1 analysis was conducted. Decision criteria currently under evaluation are the Level 1 0.5 $mg/m^3$ value for gas emissions MATE and EPC values from the MEG study, TLV's, S values, and others.

For purposes of illustration, the decision process can be conveniently described using the results of a Level 1 analysis of a stack sample collected with a SASS train, and applying two different sets of decision criteria. Table 1 lists the compound categories found in the sample and their calculated source concentrations.

Each of these concentrations can be compared with a consistent set of decision criteria. In this example, the concentration for each category is compared against the general 0.5 $mg/m^3$ gaseous emission Level 1 criterion and against the MATE values.

Column 3 show that four compound categories exceeded the 0.5 $mg/m^3$ concentration and further studies are indicated for fused aromatics above and below MW 216, heterocyclic nitrogen compounds and carboxylic acids. Column 4 lists the most stringent or "worst case" MATE values for compounds in each of the observed categories. Column 5 gives the results of comparing the observed concentrations with these MATE values. The decision process becomes more complicated when using criteria such as the MATE values because the toxicity data on which they are based are

## TABLE 1

Comparison of Level 1 Data with Decision Criteria

| Compound Categories | Observed Source Concentration (mg/m$^3$) | Exceeds Level 1 0.5 mg/m$^3$ | Worst Case MATE (mg/m$^3$) | Exceeds MATE Value |
|---|---|---|---|---|
| Aliphatic HC's | 0.06 | no | 200 | no |
| Aromatics - Benzenes | 0.06 | no | 1 | no |
| Fused Aromatics <216 | 5. | yes | 30 | no |
| Fused Aromatics >216 | 5. | yes | $2 \times 10^{-5}$ | yes |
| Heterocyclic S | 0.2 | no | 1 | no |
| Heterocyclic N | 2. | yes | 0.2 | yes |
| Heterocyclic O | 0.2 | no | 590 | no |
| Carboxylic Acids | 2. | yes | 1 | yes |
| Phenols | 0.1 | no | 2 | no |
| Esters | 0.08 | no | 5 | no |

for specific compounds and the only information one can expect from the Level 1 analysis is for categories of compounds. A "worst case" approach may be taken by using the most stringent MATE value for any compound belonging to each category as a conservative criterion for the Level 1 comparison. This is the methodology represented in Table 1.

Using these "worst case" MATE values, three categories are found to exceed the relevant MATE concentration. Using these criteria, further analysis of the lower molecular weight fused aromatics (MW < 216) is not indicated, while detailed analysis of the fused aromatics with MW > 216, the heterocyclic nitrogen and the carboxylic acid categories does appear to be necessary. The decision logic described here has been used as the underlying concept in development of the Source Assessment Models (SAM). In some cases the selection of the "worst case" MATE value as the basis for subjecting a particular chemical category to further scrutiny may prove to be an unreasonably severe criterion. A more critical examination of the Level 1 data (particularly the LRMS data) may serve to provide more reasonable and appropriate decision levels in many of those instances. This approach is currently under evaluation.

To aid the analyst in evaluating the Level 1 data for further action, Appendix A has been constructed to relate each of the MEG compounds and the chemical categories to which they are assigned, to the points at which they appear in the Level 1 analytical scheme. Again, emphasis is placed on the use of the Appendix A categorization as an aid in the analysis and interpretation of data, and not as a definitive list of compounds of concern in environmental assessment.

## III. LEVEL 2 SAMPLING AND ANALYSIS: TENTATIVE PROCEDURES

### A. Sample Types and Sampling Methods

The basic process sample types to be dealt with at each of the levels of sampling and analysis are any gases which may contain suspended liquid and/or solid particles, liquids and slurries, and solids. Level 2 analyses may be conducted either on samples freshly collected for that purpose or on samples retained from the Level 1 sampling effort. The choice between collecting a new sample or analyzing a retained sample or fraction for the Level 2 data will be highly specific to the exact question to be answered and to the nature of the chemical species to be determined. For example, the Level 2 requirement could be to confirm the presence of and determine the identity of each of several polychlorinated biphenyls (PCB's) in a source. Since the Level 1 sampling procedures are known to be adequate by Level 2 standards for collection of PCB's and since PCB's do not deteriorate in storage, it would usually be sufficient to analyze a retained Level 1 sample to provide the required data. If the Level 2 question pertained to some reactive species or to other material not collected well by the Level 1 methods, then a new specific sampling and analysis effort may be called for, using alternative procedures.

Most of the organic samples retained from the Level 1 study will be in the form of extracts in methylene chloride solution. Two exceptions are the sorbent module wash, which at present is a methanol/methylene chloride solution (or combined solution/suspension), and the "grab" gas sample. The Level 1 gas sample for determination of reactive sulfur species and low-molecular-weight hydrocarbon species will not have been retained, having been used for the on-site GC analysis. Some portions of the original solid and particulate samples may be available, since these tend to be more stable than the other samples and to be available in larger quantities than required in the minimum Level 1 procedure.

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The Level 1 samples - mostly extract solutions - are conveniently available for more comprehensive organic analytical characterization using all of the techniques discussed later. However, before proceeding to more detailed analysis of these (Level 1) samples to answer the Level 2 question, the appropriateness of the sample for study must be carefully evaluated. Does the sample provide a sufficiently quantitative representation of the source? Was the sampling procedure efficient for the species in question? Will the species to be analyzed be stable enough to warrant more detailed analysis? Would an alternative procedure provide a more interference-free sample for analysis? Each of these questions requires a specific answer in each specific instance, but the general considerations are common to all further Level 2 studies.

In many instances, the results from the Level 1 sampling and analysis study will have triggered specific Level 2 questions. In order to provide better guidance for the selection of specific Level 2 sampling and analysis procedures, further studies on the retained Level 1 samples may be warranted. These might be needed to confirm tentative identifications or to look for species that might interfere with specific methods. However, one should remember that, at best, Level 1 samples still retain all the inherent limitations designed into the selection of sample size, collection methods and extraction procedures. In Level 1, not all categories or species are collected in an optimum manner, since the procedure is required to make certain compromises in the interest of economy and generality. This statement is not a criticism of the Level 1 procedures but rather a reminder that a single set of procedures which attempts to encompass all possible species cannot be expected to be optimized for each specific species or category.

It will be necessary in many cases to collect additional samples for Level 2 studies. The reasons for this include the arguments above about possible limitations of the samples retained from Level 1 and especially, perhaps, the need for providing a more accurate quantitative representation of the entire composition of an effluent or process stream. A new Level 2 sample might also be designed to meet a requirement for quantitative accuracy for specific compounds such as the polynuclear aromatic hydrocarbons (PAH's) aldehydes, phenols, nitrosoamines, etc. The sampling methods available for various categories of sources and compounds are discussed in the following chapter.

## B. Analysis Methods

This section describes specific procedures which are provisionally recommended for Level 2 studies. Two basically different types of Level 2 studies may be carried out. In most cases, results from the Level 1 study will have provided chemical class information which will have directed attention to specific compound categories. In those cases a specific sampling and analysis procedure may be selected. Recommendations for such procedures organized ,for purposes of illustration, around the MEG categories, are given in Subsection 1 below. In some other cases, a need for Level 2 studies may be indicated by criteria such as a set of positive biotest results, rather than chemical composition data. The biotest results would not be expected to target specific chemical categories for study in Level 2. In these cases a comprehensive set of Level 2 studies will be required, possibly using procedures with lower detection limits than those of Level 1. It may also be necessary to analyze for species which may originally have gone undetected because of the procedural constraints imposed by the Level 1 economic considerations. A general approach to analysis of these samples of unknown composition is discussed in Subsection 2 of this section.

### 1. Compounds in Predetermined Categories

It is expected that most Level 2 organic analyses will be directed towards one or more specific classes of chemical compounds that were indicated by Level 1 analysis to exceed their respective decision-level concentration(s). The Multimedia Environmental Goals (MEG) list (8) provides a classification of organic species into 25 chemically diferentiated categories, and is therefore a convenient means of organizing approaches to Level 2 sampling and analysis. This organizational approach does not mean, of course, that only the particular chemical compounds on the MEG list are to be sought for in Level 2 analyses. Furthermore, it is recognized that there are a few kinds of organic compounds (e.g., pesticides, insecticides, phosphates, silicones) that do not fit logically into any of the 25 MEG categories and that must therefore be considered separately.

It now seems clear, nevertheless, that most Level 2 questions will be able to be formulated in terms of determining the identity and abundance of compounds within chemical categories that correspond fairly closely to those of the MEG list. Sampling and analysis methods on which tentative Level 2 procedures are based are described in Chapter IV and V of this report. Tables 1 and 2 summarize the particular choices of sampling and analysis methods, respectively, that can be recommended for Level 2 analyses by MEG category. The appropriate methods will, in some cases, be described in somewhat more detail in the final Level 2 Procedures Manual. However, because each Level 2 study is likely to be unique in some respects, it is necessary to allow for flexibility and to leave exact details--sample size, GC temperature program, etc.--to the discretion of the analyst.

## TABLE 2

### Level 2 Preferred Sampling and Sample Treatment Methods for Various Organic Chemical Categories

| | Gaseous Streams | | Aqueous Streams | |
|---|---|---|---|---|
| Chemical Categories | Sampling | Treatment | Sampling | Treatment |
| Aliphatic Hydrocarbons | | | | |
| $C_1 - C_7$ | gas bulb or solid sorbent | none, or adsorb to concentrate | grab | purge & trap pentane |
| $>C_7$ | SASS | resin adsorbtion | proportional | pentane extraction |
| Alkyl Halides | | | | |
| b.p. <100°C | gas bulb or solid sorbent | none or adsorb to concentrate | grab | purge & trap |
| b.p. >100°c | SASS | resin adsorption | proportional | $CH_2Cl_2$ extraction |
| Ethers | SASS | resin adsorption | proportional | $CH_2Cl_2$ extraction |
| Halogenated Ethers | | | | |
| b.p. <100°C | gas bulb | none, or adsorb to concentrate | grab | purge & trap |
| b.p. >100°C | SASS | resin adsorption | proportional | $CH_2Cl_2$ extraction |
| Alcohols | | | | |
| b.p. <100°C ($\leq C_4$) | gas bulb | none, or adsorb to concentrate | grab | purge & trap |
| b.p. >100°C | SASS | resin adsorption | proportional | resin adsorption or other extraction |
| Glycols, epoxides | SASS | resin adsorption | grab or proportional | none, or ether extraction |
| Aldehydes | | | | |
| b.p. <100°C ($\leq C_5$) | Bisulfite impingers | none | grab | purge & trap |
| b.p. >100°C | SASS | resin adsorption | proportional | ether extraction |
| Ketones | | | | |
| b.p. <100°C ($\leq C_4$) | gas bulb | none, or adsorb to concentrate | grab | purge & trap |
| b.p. >100°C | SASS | resin adsorption | proportional | $CH_2Cl_2$ extraction |
| Carboxylic Acids | | | | |
| formic, acetic | SASS | resin adsorption | grab | purge & trap |
| $C_3 - C_5$ | SASS | resin adsorption | grab | none |
| $>C_5$ | SASS | resin adsorption | proportional | $CH_2Cl_2$ extraction at $pH_2$ |

TABLE 2
(continued)

| Chemical Categories | Gaseous Streams |  | Aqueous Streams |  |
|---|---|---|---|---|
|  | Sampling | Treatment | Sampling | Treatment |
| Amides |  |  |  |  |
| $<C_9$ | SASS | resin adsorption | grab | none |
| $>C_9$ | SASS | resin adsorption | grab | ether extraction |
| Esters | SASS | resin adsorption | grab | $CH_2Cl_2$extraction |
| Nitriles |  |  |  |  |
| b.p. <100°C ( $C_2$) | gas (reactive) | none, or adsorb to concentrate | grab | purge & trap |
| $<C_6$ | SASS | resin adsorption | grab | none |
| $>C_6$ | SASS | resin adsorption | proportional | $CH_2Cl_2$extraction |
| Amines |  |  |  |  |
| b.p. <100°C | gas bulb | none, or adsorb to concentrate | grab | none |
| b.p. >100°C ($\leq C_6$) | SASS | resin adsorption | grab | none |
| ($>C_6$) | SASS | resin adsorption | grab | $CH_2Cl_2$extration at $pH_{11}$ |
| Azo compounds, hydrazine, etc. | special reagent impingers | none | grab | none, or $CH_2Cl_2$ extraction at $pH_{11}$ |
| Nitrosamines | SASS | resin adsorption | grab | none, or $CH_2Cl_2$ extraction at $pH_{11}$ |
| Mercaptans | gas bulb and on-site GC | none, or adsorb to concentrate | grab | none |
| Sulfides, Disulfides |  |  |  |  |
| b.p. <100°C ($\leq C_4$) | gas bulb | none, or adsorb to concentrate | grab | purge & trap |
| b.p. >100°C | SASS | resin adsorption | proportional | $CH_2Cl_2$extraction |
| Sulfonic Acids, Sulfoxides | SASS | resin adsorption | grab | none |
| Benzene, Substituted Benzene Hydrocarbons |  |  |  |  |
| b.p. <100°C | gas bulb | none, or adsorb to concentrate | proportional | $CH_2Cl_2$extraction |
| b.p. >100°C | SASS | resin adsorption | proportional | $CH_2Cl_2$extraction |
| Halogenated Aromatics | SASS | resin adsorption | proportional | $CH_2Cl_2$extraction |

TABLE 2
(continued)

| Chemical Categories | Gaseous Streams |  | Aqueous Streams |  |
|---|---|---|---|---|
|  | Sampling | Treatment | Sampling | Treatment |
| Aromatic Nitro Compounds | SASS | resin adsorption | proportional | $CH_2Cl_2$extraction |
| Phenols<br>Halophenols<br>Nitrophenols | SASS | resin adsorption | proportional or grab | none, or (for $>C_{10}$) ether extraction at $pH_2$ |
| Fused Polycyclic Hydrocarbons Fused Non-Alternant Polycyclic Hydrocarbons | SASS | resin adsorption | proportional | $CH_2Cl_2$extraction |
| Heterocyclic Nitrogen Compound | SASS | resin adsorption | grab | $CH_2Cl_2$extraction at $pH_{11}$ |
| Heterocyclic Oxygen Compounds |  |  |  |  |
| b.p. <100°C (Furan) | gas bulb | none, or absorb to concentrate | grab | purge & trap |
| b.p. >100°C | SASS | resin adsorption | proportional | $CH_2Cl_2$extraction |
| Heterocyclic Sulfur Compounds |  |  |  |  |
| b.p. <100°C (Thiphene) | gas bulb | none, or adsorb to concentrate | proportional | solvent extraction |
| b.p. >100°C | SASS | resin adsorption | proportional | solvent extraction |

TABLE 3

Level 2 Analysis Methods by MEG Category

| No. | MEG Category/Subcategory | Analysis Method |
|---|---|---|
| 1 | Aliphatic Hydrocarbons | |
| | b.p. < 100°C | GC/ms or GC/FID on Porapak Q |
| | b.p. > 100°C | GC/ms or GC/FID on SP-2250 (or OV-17) |
| 2 | Alkyl Halides | |
| | b.p. < 100°C | GC/ms or GC/ECD (isothermal) on Porapak Q |
| | b.p. > 100°C | GC/ms or GC/ECD (isothermal) on SP-2250 (or OV-17) |
| 3 | Ethers | GC/ms on SP-1000 |
| 4 | Halogenated Ethers | GC/ms or GC/ECD (isothermal) on SP-1000 |
| 5 | Alcohols | GC/ms on SP-1000 |
| 6 | Glycols, epoxides | GC/ms on Porapak P (direct aqueous injection) |
| 7a | Aldehydes | 1. Iodometric titration of bisulfite impingers or<br>2. GC/ms on SP-1000 |
| 7b | Ketones | GC/ms on SP-1000 |
| 8a-b | Carboxylic Acids | 1. Reverse phase HPLC or<br>2. GC/ms on SP-1000 after formation of derivative |
| 8c<br>8d | Amides<br>Esters | 1. Normal or reverse phase HPLC or<br>2. GC/ms on SP-1000 |
| 9 | Nitriles | GC/ms on SP-1000 |
| 10<br>11 | Amines<br>Azo compounds | GC/ms on Carbowax 20M-0.8% KOH |
| 12 | Nitrosamines | 1. Normal phase HPLC or Gel Permeation Chromatography or<br>2. GC/ms on SP-1000 or Tenax |

## TABLE 3
(continued)

| No. | MEG Category/Subcategory | Analysis Method |
|---|---|---|
| 13 | Mercaptans, Sulfides and Disulfides | 1. GC/FPD on Teflon/polyphenyl ether/$H_3PO_4$ (in field for reactive species) or<br>2. GC/ms on OV-17 or SP-1000 |
| 14 | Sulfonic Acids, | Ion-pair HPLC |
|  | Sulfoxides | Normal or reverse phase HPLC |
| 15 | Benzene, Substituted Benzene Hydrocarbons | GC/ms or GC/FID on SP-2250 (or OV-17) |
| 16 | Halogenated Aromatics | GC/ms or GC/ECD (isothermal) on SP-2250 (or OV-17) |
| 17 | Aromatic Nitro Compounds | 1. Reverse phase HPLC or<br>2. GC/ms on SP-1000 or SP-2250 |
| 18<br>19<br>20 | Phenols<br>Halophenols<br>Nitrophenols | 1. Reverse phase HPLC or<br>2. GC/ms on Tenax (direct aqueous injection) or<br>3. GC/ms on SP-1000 after derivative formation |
| 21<br>22 | Fused Polycyclic Hydrocarbons<br>Fused Non-Alternant Polycyclic Hydrocarbons | 1. GC/ms on Dexsil 400 or<br>2. Reverse or normal phase HPLC |
| 23<br>24<br>25 | Heterocyclic Nitrogen Compounds<br>Heterocyclic Oxygen Compounds<br>Heterocyclic Sulfur Compounds | 1. GC/ms on SP-1000 or SP-2250 or<br>2. Normal phase HPLC |

### 2. Unknown Samples

Samples to be analyzed at Level 2 for which Level 1 failed to provide a more directed analysis will generally have to be analyzed by methods that have greater detection sensitivity for specific compounds (i.e., lower detection limits) than those used in Level 1, and that deal better with those areas for which Level 1 procedures are least well suited, for instance gases and high molecular weight species. It will be important to provide assurance that no significant portion of the collected sample has failed to be accounted for in the analysis, and that qualitative detail is adequate to meet the requirements of the inquiry.

It is difficult to devise a specific scheme that will be appropriate for all process streams to be analyzed in this manner. This section seeks to present some general guidance and suggestions of procedures to be used and the sequence in which they should be used.

A general scheme that should be useful in planning a Level 2 analysis is given in Figures 1.a. and 1.b. Three general types of samples are considered; (1) those that are essentially gaseous, but may contain suspended solid or liquid aerosols; (2) those that are essentially liquid -- often aqueous -- but that may contain dissolved gases, liquids and solids as well as suspended solid particles; and (3) those that are principally solid, and which may contain some entrained liquids.

In terms of the sampling characteristics of the SASS train, "gases" are defined as species with a boiling point below 100°C. "Vapors" are defined as species whose boiling points are above 100°C (at 760 mm), and that are present in the gas phase at partial pressures below their saturation vapor pressures. The term "particulate" includes liquid aerosols and solid particles. Details of some provisional sampling and analysis procedures for these species are given in Chapters IV and V.

Samples from the gas phase (e.g., from stacks, ducts and ambient air) are expected to be collected principally by direct "grab" sampling, using plastic bags, and by the SASS train or similar devices, such as, for example, the modified Method 5 train. The "grab" samples may be analyzed directly, using appropriate GC and/or GC/MS techniques, or they may be pre-concentrated by adsorption at low temperature on resins such as Tenax-GC, from which they can be thermally desorbed for GC and/or GC/MS analysis.

The samples collected by an atmospheric sampling train such as SASS will pass through the cyclones and filters that are included in those systems to remove and collect suspended solids, and will then be led through a sorbent resin trap (XAD-2) to collect vapors of organic compounds. Some organic vapors will be condensed on the walls of the SASS train components and some condensate may collect in a sump below the sorbent trap. These condensates will be added to the extract obtained from treatment of the sorbent resin with methylene chloride.

The particulate matter collected in the cyclones and on the filter of the sampling train should be examined microscopically for evidence of intact crystalline species whose identity might subsequently be obsured or lost in the ensuing separation treatments. Optical microscopy may be usefully combined with x-ray and/or electron diffraction and other microscopic analysis techniques wherever the examination of individual particles may be deemed appropriate in the general analytical scheme. After microscopic examination, the particulate catch will be extracted with methylene chloride or other suitable solvent and the extract, together with that from the sorbent trap, submitted to analysis by the general scheme outlined in Figure 1.b. for organic liquids. The residue, which may contain insoluble organic as well as inorganic components, should be subjected to analysis by infrared (IR), thermogravimetric analysis (TGA) and by high resolution mass spectrometry (HRMS), using a "probe" sample insertion technique.

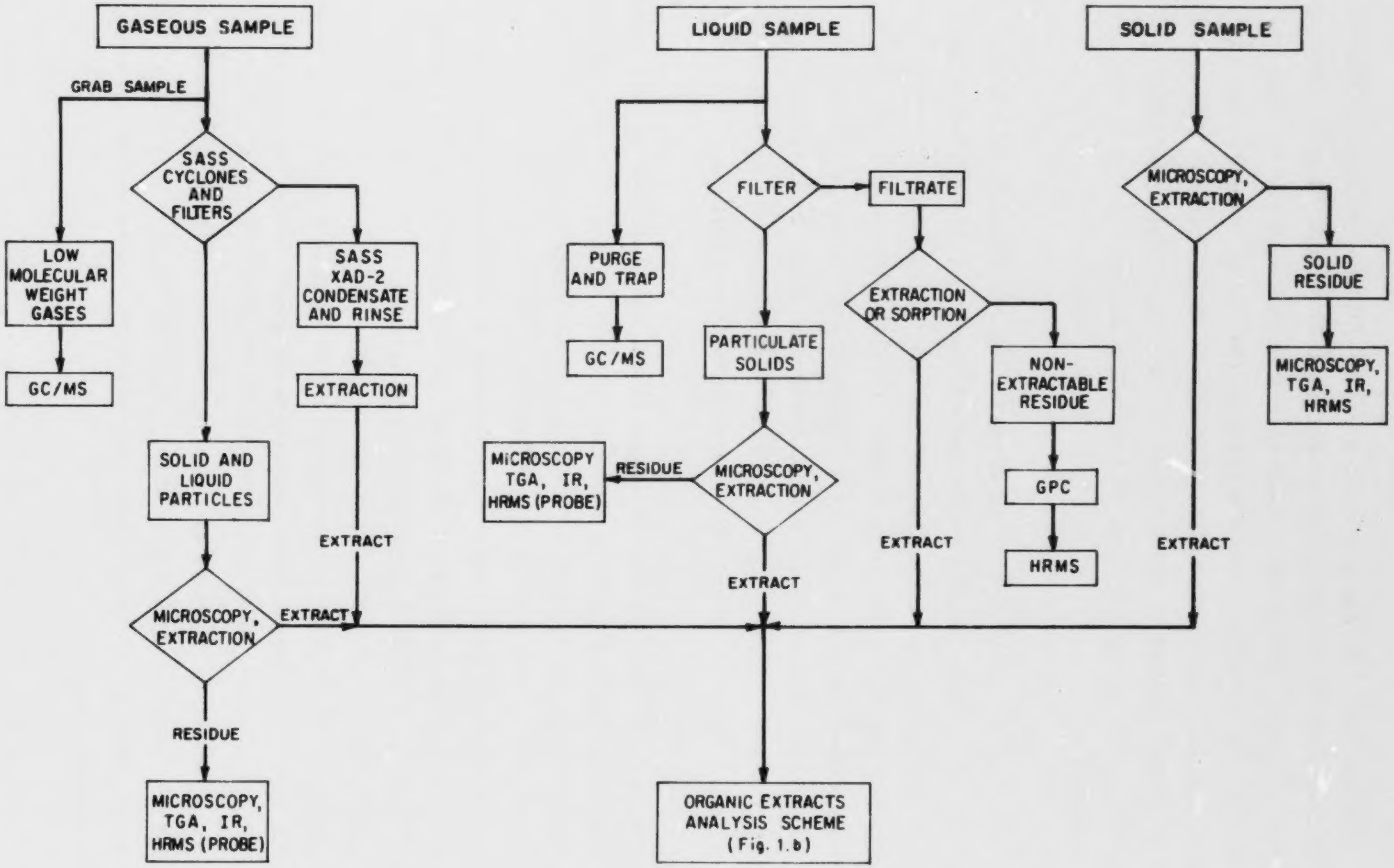

GASEOUS SAMPLE
GRAB SAMPLE
SASS CYCLONES AND FILTERS
LOW MOLECULAR WEIGHT GASES
GC/MS
SASS XAD-2 CONDENSATE AND RINSE
EXTRACTION
SOLID AND LIQUID PARTICLES
EXTRACT
MICROSCOPY, EXTRACTION
EXTRACT
RESIDUE
MICROSCOPY, TGA, IR, HRMS (PROBE)
LIQUID SAMPLE
FILTER
FILTRATE
PURGE AND TRAP
GC/MS
PARTICULATE SOLIDS
EXTRACTION OR SORPTION
NON-EXTRACTABLE RESIDUE
MICROSCOPY TGA, IR, HRMS (PROBE)
RESIDUE
MICROSCOPY, EXTRACTION
GPC
EXTRACT
EXTRACT
HRMS
SOLID SAMPLE
MICROSCOPY, EXTRACTION
SOLID RESIDUE
MICROSCOPY, TGA, IR, HRMS
EXTRACT
ORGANIC EXTRACTS ANALYSIS SCHEME (Fig. 1.b)

FIGURE 1.a. LEVEL 2 ORGANIC ANALYSIS SCHEME.

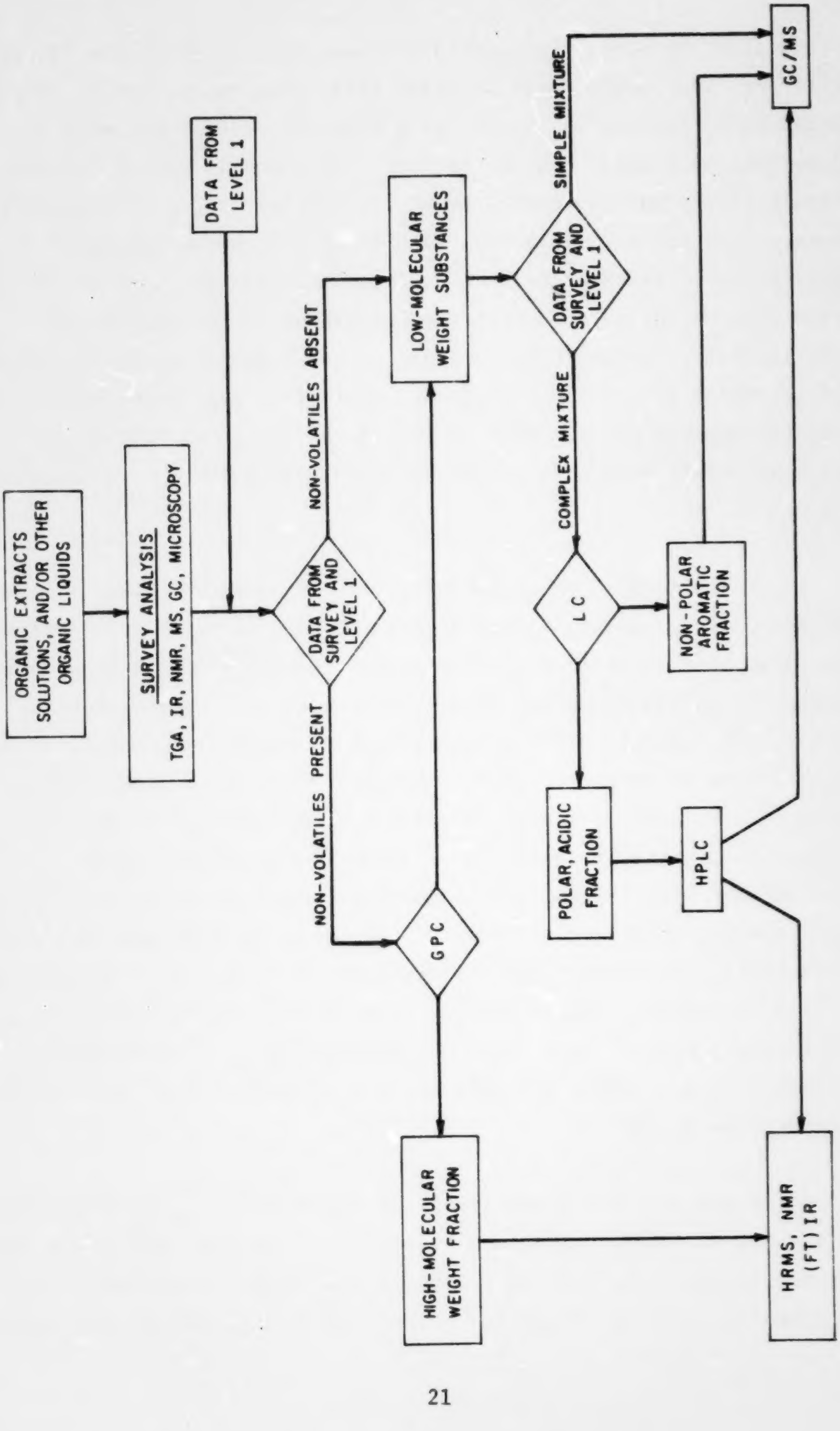

ORGANIC EXTRACTS SOLUTIONS, AND/OR OTHER ORGANIC LIQUIDS
SURVEY ANALYSIS
TGA, IR, NMR, MS, GC, MICROSCOPY
DATA FROM LEVEL 1
DATA FROM SURVEY AND LEVEL 1
NON-VOLATILES ABSENT
NON-VOLATILES PRESENT
LOW-MOLECULAR WEIGHT SUBSTANCES
GPC
HIGH-MOLECULAR WEIGHT FRACTION
DATA FROM SURVEY AND LEVEL 1
SIMPLE MIXTURE
COMPLEX MIXTURE
LC
NON-POLAR AROMATIC FRACTION
POLAR, ACIDIC FRACTION
HPLC
GC/MS
HRMS, NMR (FT) IR

FIGURE 1.b. ORGANIC EXTRACTS ANALYSIS SCHEME.

Samples collected from liquid streams, most of which are likely to be aqueous and destined for dilution into groundwater, may be sampled batchwise or by continuous contact of a diverted side stream with a solid sorbent or a continuous extractant. As shown in Tables 1 and 2, the liquid sample may preferably be analyzed directly for some organic components, but for most purposes, filtration (to remove suspended solids), followed by extraction in an immissible solvent such as methylene chloride will be the method of choice for preparing the sample for organic analysis. In any event a separate batch sample should be taken initially, which will be purged with a nonreactive gas to remove and collect low-boiling organic gases. This collected gas sample is then to be analyzed by GC/MS, similarly to the "grab" sample taken from a gaseous stream.

After filtration, the liquid filtrate of an aqueous sample should be extracted with a suitable organic solvent such as methylene chloride, having first been adjusted to a high pH and then to a low pH to promote extraction of partially dissociated ionic substances. Alternatively, contact of the aqueous filtrate with a sorbent resin may prove to be a preferable general method to remove organics which may subsequently be desorbed by a suitable solvent. In either case, the organic extract will then be subjected to analysis as shown in Figure 1.b. above, and the residue will be analyzed by gel-permeation chromatography (GPC) and HRMS (probe) to detect and identify any organics that were not able to be extracted or sorbed. Any solid residue that remains after filtration of a principally liquid sample, will be analyzed in the same way as particulates removed from a gaseous stream, i.e., by microscopy, extraction with an organic solvent, and TGA, IR and HRMS analysis of the non-extractable residue.

Solid samples, which are likely to be particulate, and which may contain small amounts of entrained liquids, will be analyzed in the same manner as the solid particulate fractions removed by filtration from gaseous samples and liquid samples. The organic extracts of these samples can be expected to dissolve and remove any entrained organic liquids as well as the soluble portion of the solids themselves. These extracts will then be analyzed in the same manner as all other organic extracts.

The general analytical scheme for organic extracts rinse solutions and other organic liquids is shown in Figure 1.b. When the information sought is not limited to a specific question about one or a few components, but requires instead a broad-ranging examination of the entire organic composition of the sample, an initial survey analysis should be performed prior to the application of various chromatographic separation techniques. Data may be obtained from TGA, IR, MS, GC and microscopic examination of residues remaining upon evaporation of the solvent (typically methylene chloride or similar low-boiling solvent) at a temperature not above 40°C. These data, in combination with NMR, which requires that a portion of the sample be redissolved in an appropriate solvent (aprotic for proton-NMR; $^{13}$C-depleted for $^{13}$C-NMR, etc), will serve to show what the general composition of the sample is, whether it is especially complex or limited to a relatively small number of components, and whether it contains high-molecular-weight and/or non-volatile organic species which might not be seen in a TCO assay. Any other relevant data, including that from a prior Level 1 study should be considered here, in the interest of developing the most efficient and productive plan for the subsequent separation and identification scheme.

On the basis of the survey analysis, a decision can be made as to whether a significant fraction of the sample appears to be of such low volatility that it will not be susceptible to analysis by GC/MS. If so, the entire sample should first be subjected to gel-permeation chromatography (GPC) to separate the high-molecular weight fraction, which is likely to contain many or all of the non-volatiles, from the relatively low-molecular-weight substances. A break-point of M.W. ≈ 300-500 is likely to be satisfactory for the GPC separation. The high-molecular weight, non-volatile fraction is likely to be analyzed most successfully by a combination of NMR and IR (both Fourier-transformassisted) and perhaps by HRMS, using a solids probe for sample insertion.

If the low-molecular-weight and relatively more volatile fraction from GPC (or the entire sample if GPC was not required) appears to be a mixture of only a few substances, as suggested by the survey data, GC/MS may be sufficient to provide all the identification and quantification required. If not, then an LC separation, using silica gel, alumina or Florisil, as appropriate, will be necessary to resolve the mixture into more manageable fractions, as well as to assist in characterizing chemical composition. Chapter V of this manual provides a more detailed discussion of liquid chromatographic techniques that will be most appropriate to this operation.

Non-polar and aromatic fractions of the LC eluate may be submitted directly to GC/MS. Those that are more polar and acidic may benefit from a more discrete resolution of their components by means of high performance liquid chromatography (HPLC). The choice of a favorable combination of column packing, mobile phase and detector will depend in part on information available to the analyst about the sample at this point in the process and partly on the analyst's own experience and preference. Since HPLC techniques are often capable of resolving individual chemical substances, discrete fractions may be collected for subsequent analysis by HRMS, (FT) NMR, and/or (FT) IR, or by GC/MS. More detailed descriptions of these analytical techniques, with particular reference to their applicability to environmental assessment studies, are provided in Chapter V of this manual.

## IV. SAMPLING METHODS

Sampling methods for use in Level 2 may in many cases be the same as those used in Level 1. It may be possible in some cases where a specific measurement is sought to use simpler procedures than those prescribed for Level 1. In some cases, alternative procedures will be desirable to measure species not represented well by the Level 1 scheme and/or especially reactive compounds, such as certain reactive olefins, hydrazines, etc.

The available sampling methods have been described in detail in several sources. All of the Level 1 sampling methods and procedures are described in the "IERL-RTP Procedures Manual: Level 1 Environmental Assessment". (3) A companion document, "Technical Manual for Process Sampling Strategies for Organic Materials", (4) gives further details on Level 1 methods and additional methods that may be appropriate to Level 2 and Level 3 studies. Many specific methods are detailed in various ASTM documents, and the Federal Register contains descriptions of standardized EPA methods. The reference "Standard Methods for the Examination of Water and Wastewater", (16) and the EPA publication, "Handbook for Monitoring Industrial Wastewater" (17) are excellent resources for water sampling and analysis methods. Fugitive sampling methodology has recently been addressed in several EPA publications. (7a, 7b, 7c). The reader should refer to these and similar sources for detailed descriptions and discussions of specific methods. Those procedures which seem to be most appropriate for Level 2 studies will be reviewed briefly in this chapter. The orientation in selection of methods for consideration was influenced by the existing Level 1 procedures and the chemical categories represented in the MEG list of organic compounds.

Although it is possible and desirable to specify a restricted set of procedures for Level 1 studies, the Level 2 situation is not analogous. The objectives of studies at Level 2 may cover a wide range and may vary from the need for better process (flow) data to compound-specific emission or composition data. A set of methods must be put together for the Level 2 study which are most appropriate for each specific task. Generally speaking, it should be possible to choose from the sampling methods described in this Manual, although it may be desirable in some cases to make modifications of the procedures. Methods for some species are not yet well developed and will need to continue to evolve as the state-of-the art advances.

Sources to be sampled may be organized by procedures into:

a) fixed sources: process and effluent streams, vents and stack emissions, and
b) fugitive emissions.

The sources will yield the basic sample types described as:

gas/vapor
particulate
liquid/slurry
solid

For the purposes of this Manual, particulates will be treated separately from the gases and vapors, although "particulate" refers to solid or liquid materials entrained in gaseous streams. Fugitive sources of particulates and vapors/gases are treated separately. Level 2 procedures for reactive compounds are also treated in a separate section.

## A. Gases and Vapors

### 1. Gases

The Level 1 procedure for gases involves sampling (in a bulb) followed by on-site GC analysis. Gases are considered to be those species with a boiling point range similar to those of the $C_1$ - $C_7$ hydrocarbons, i.e., -160°C to 100°C. Special provision is also made to measure the reactive reduced sulfur species on the on-site GC, using the FPD.

The disadvantage of the Level 1 procedure for the low-boiling materials is that qualitative chemical information cannot be obtained beyond that which might be inferred from the retention time data. Exoneration of a source on the basis of such limited information would require a risky assumption in many environmental assessment studies of sources of unknown composition. As an alternative, most compounds in the low boiling range, with the exception of certain reactive species, may be readily and reliably identified and quantitatively estimated by GC/MS analysis methods. The question then is of the most appropriate method for collecting the gas sample for the GC/MS study. At this point, it should be noted that experience with the Level 1 procedures -- both in terms of materials collected efficiently on the XAD-2 module and those lost in sample treatment steps -- suggests that all species boiling in the range of -160°C to 100°C ($C_1$- $C_7$ hydrocarbon equivalent) should be treated as gases.

In terms of the analysis method detection limits, it will be sufficient for Level 2 purposes in most cases to analyze the equivalent of 0.1 - 1.0 L of gas sample. It may be possible to collect grab or time-integrated samples in inert bags, as suggested by Figure 2. The bag could then be returned to the laboratory where it may be analyzed either directly or by preliminary concentration of the species on a material such as Tenax GC and subsequent thermal desorption. There are

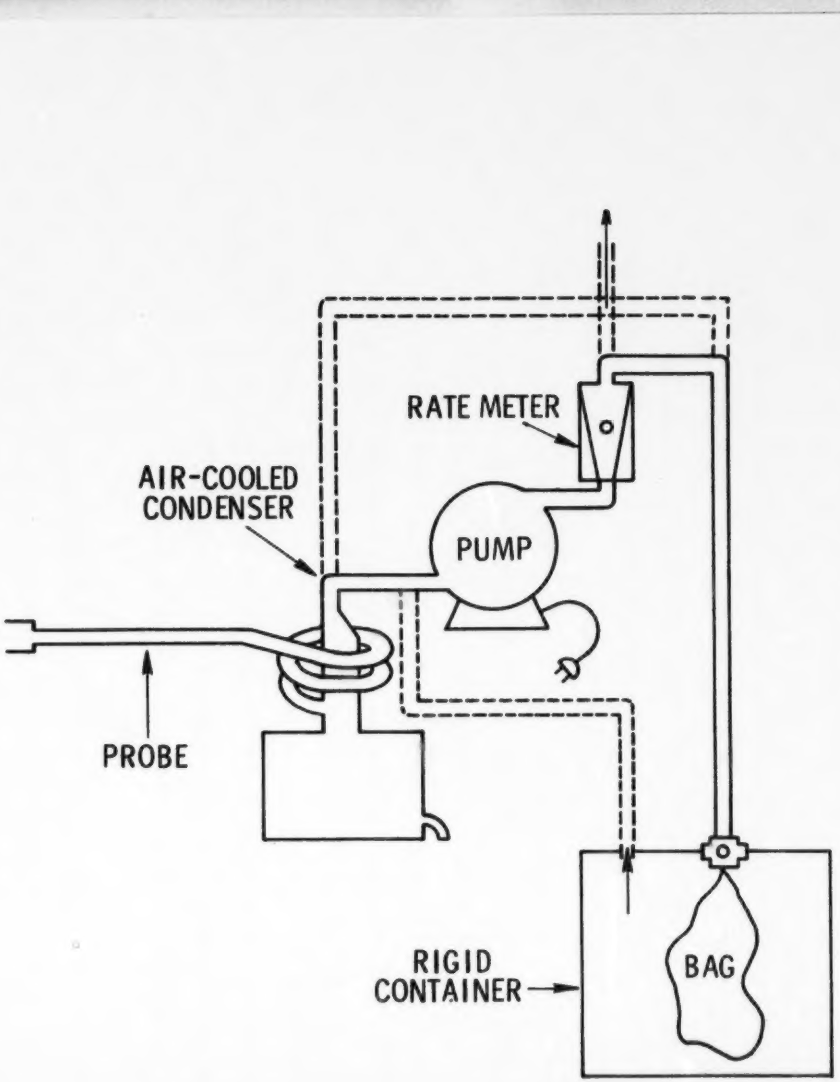

RATE METER
AIR-COOLED CONDENSER
PUMP
PROBE
RIGID CONTAINER
BAG

Figure 2 Integrated gas sampling train (Solid lines showing normal arrangement, Dotted lines - alternate arrangement, evacuating chamber around bag).

Source: EPA-600/2-76-122, April 1976 p.60

reports of the successful use of this method. The need to concentrate the samples will be set by the concentration of the species present in the sample and the detection limits of the analytical instrumentation. The major uncertainty with this approach is of the stability of samples in "inert" bags, a topic still under investigation.

An alternative method for sampling these low molecular weight materials is the use of porous polymers. Two materials in particular, XAD-2 and Tenax-GC, have been used successfully for this purpose. The choice of methodology depends on the sampling temperature, trap size and the elution volume (Vg - the volume of gas in which the compound "breaks through" the trap) of the compound. If the higher-boiling end of the volatile range (e.g. B.P.- 0°C - 100°C) is being examined, or if the concentration of volatiles is high (allowing, therefore, lower volumes of sample to satisfy the analytical detection limits), then a simple sampling system as shown in Figure 3 could be used. Tenax-GC would be the adsorbent of choice in this sampler because its higher thermal stability would facilitate direct thermal desorption and analysis. In order to obtain adequately representative quantitative data for the stream, several 0.1 - 1.0 L samples should be collected. Larger samples may be needed if greater sensitivity is demanded.

If the Vg value for solid sorbent sampling is too low at ambient (20°C ± 5°C) temperatures, then an approach using the Kaiser tube thermal gradient on a porous polymer might be used, as shown in Figure 4. While this approach has great promise from a theroetical viewpoint, preliminary field treatments have met with limited success, due to difficulty in maintaining a uniform, high temperature gradient across the Kaiser tube.

No good procedures for concentration of sufficient quantities of gaseous species for biotesting have been identified. The best

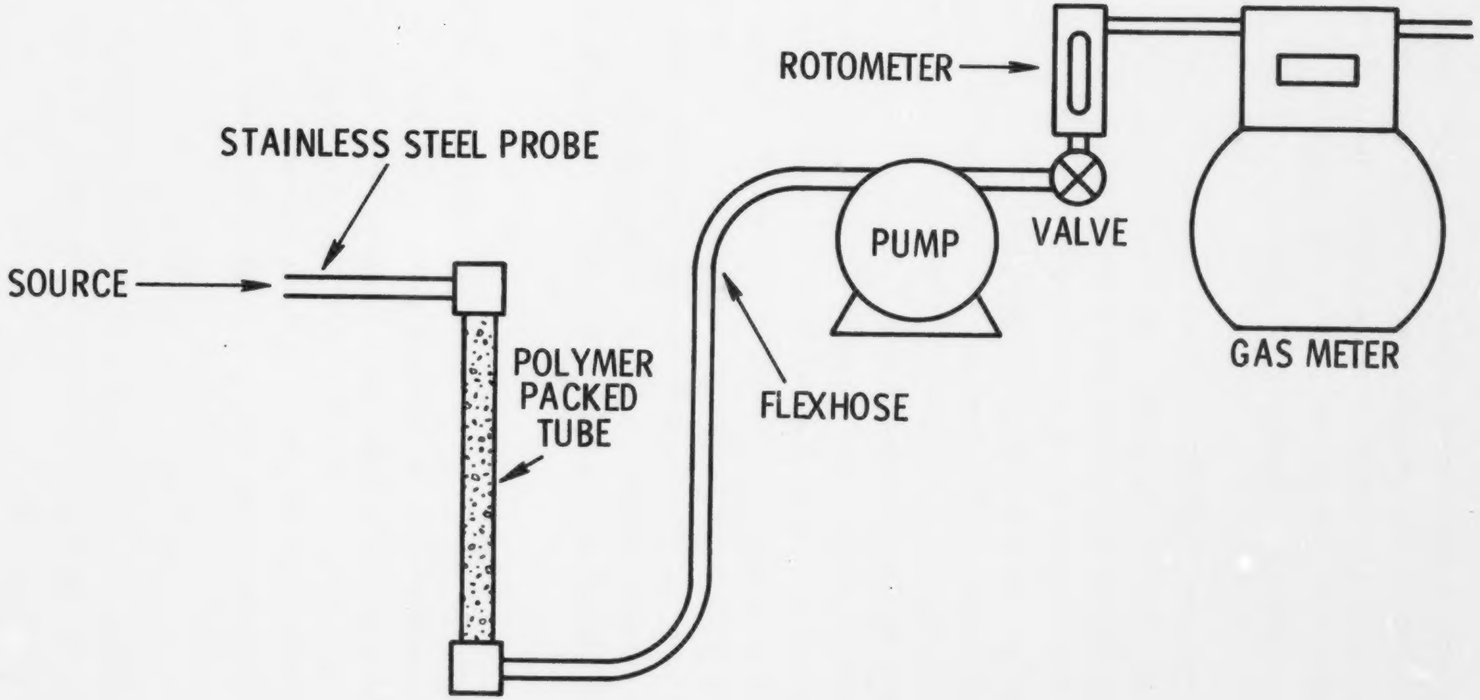

STAINLESS STEEL PROBE
SOURCE
POLYMER PACKED TUBE
FLEXHOSE
PUMP
ROTOMETER
VALVE
GAS METER

Figure 3 Porous polymer vapor sampling method

Source: EPA-600/2-76-122, April 1976 p.66

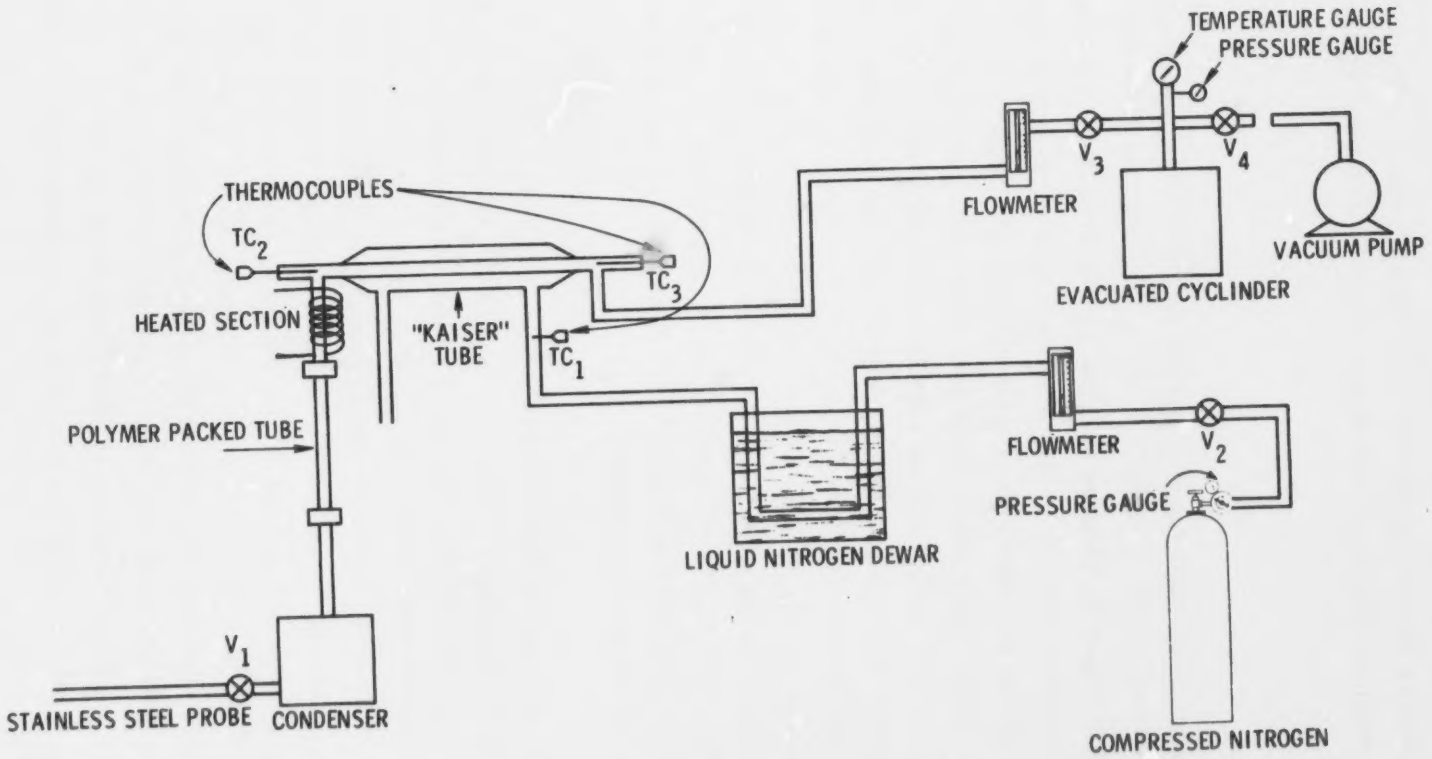

TEMPERATURE GAUGE
PRESSURE GAUGE
THERMOCOUPLES
$TC_2$
$TC_3$
$TC_1$
FLOWMETER
$V_3$
$V_4$
VACUUM PUMP
EVACUATED CYCLINDER
HEATED SECTION
"KAISER" TUBE
POLYMER PACKED TUBE
FLOWMETER
$V_2$
PRESSURE GAUGE
LIQUID NITROGEN DEWAR
$V_1$
STAINLESS STEEL PROBE
CONDENSER
COMPRESSED NITROGEN

Figure 4 Porous polymer and thermal gradient sampling train

Source: EPA-600/2-76-122, April 1976 p. 28

procedure currently available is the collection of the 3 x 500-liter bag samples, which is the sampling method required for the "stress ethylene" test.

### 2. Vapors

In the context of this report, vapors are defined as compounds with boiling points above about 100°C (or a $C_8$ normal hydrocarbon equivalent) that exist as gaseous species in the stream or environment to be sampled because they are present below their equilibrium vapor pressure concentration. When these same species are present at concentrations above their vapor pressures they would, of course, exist as aerosols and be sampled as particulate. Most of the compounds, in the vapor range are sampled efficiently by the XAD-2 sorbent module (Figure 5) in the SASS train (see Figure 7). For those compounds with low Vg values (e.g., boiling points below 20°C), it may be necessary to sample less than 30 cubic meters (the Level 1 volume) to ensure quantitative collection. These constraints are discussed in detail in the EPA report, "Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds". (6)

The preferred Level 2 sampling procedure for organic (and organometallic) vapors is the use of XAD-2 or Tenax GC. Alternative methods should only be used when there are data to show an established preference over these materials. The resins can be used with the sorbent module of the SASS train alone (no particulates, no impingers) when sufficient quantities are required for biotests. XAD-2 is the preferred resin when solvent extraction procedures are to be used in sample preparation. If thermal desorption is to be used, Tenax GC is the sorbent of choice. Thermal desorption methods should generally be reserved for small-scale sampling apparatus. While XAD-2 and Tenax-GC have comparable Vg characteristics at 20°C, XAD-2 has generally slightly better volumetric capacity and has substantially greater (10X) weight capacity than Tenax-GC.

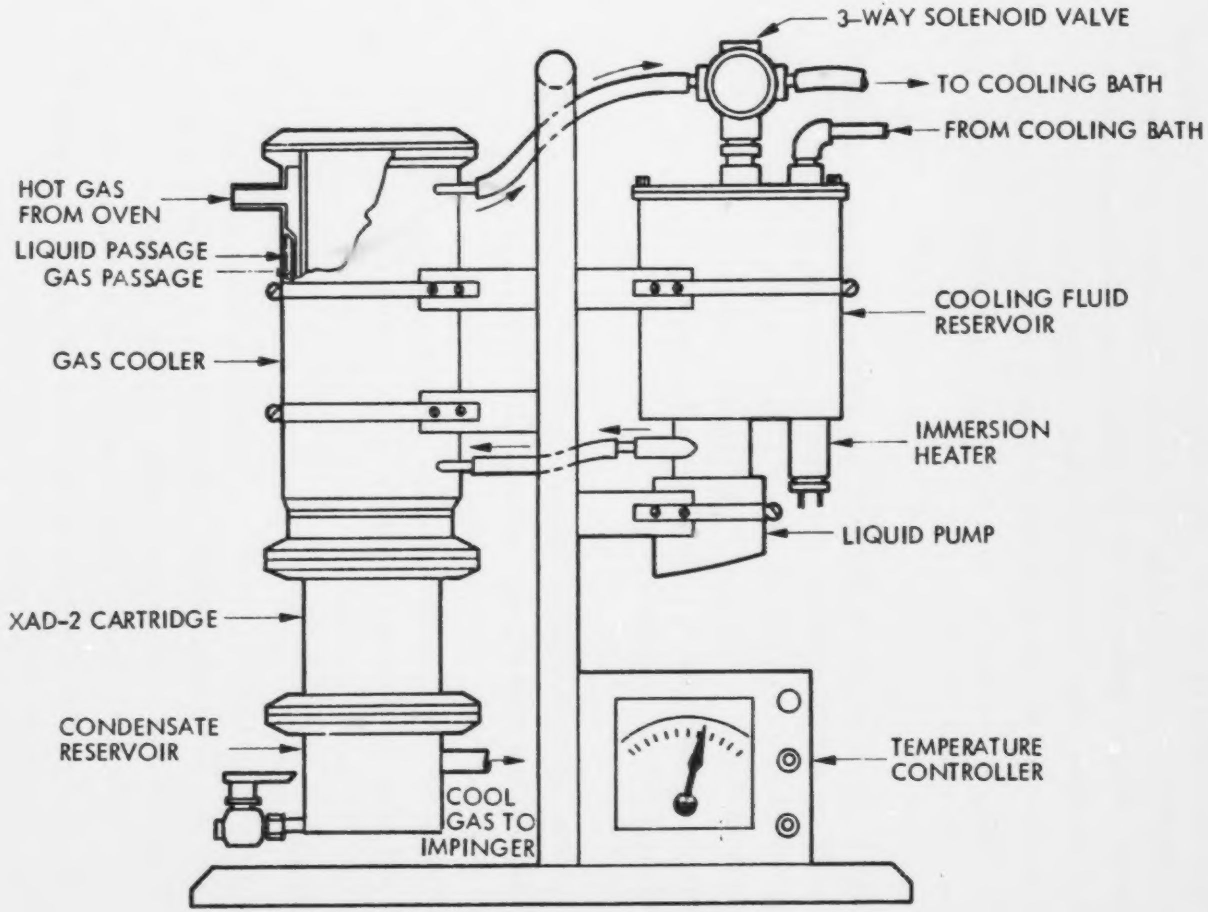

3-WAY SOLENOID VALVE
TO COOLING BATH
FROM COOLING BATH
HOT GAS FROM OVEN
LIQUID PASSAGE
GAS PASSAGE
COOLING FLUID RESERVOIR
GAS COOLER
IMMERSION HEATER
LIQUID PUMP
XAD-2 CARTRIDGE
CONDENSATE RESERVOIR
TEMPERATURE CONTROLLER
COOL GAS TO IMPINGER

Figure 5 XAD-2 Sorbent Trap Module

Source: EPA-600/2-76-160a, June 1976 p. 32

In many Level 2 cases it will be possible to use simpler sampling methods than the SASS train when only organic vapors are to be measured. In earlier studies reported in the literature, impingers and bubblers using toluene, xylene, isooctane or ethylene glycol have been used to sample, for instance, PCB's and pesticides. NIOSH methods use activated petroleum-base charcoal and activated coconut-base charcoal for a wide range of compounds. Many other resins related to XAD-2 and Tenax GC have also been studied. (6)

Smaller scale versions of the SASS sorbent module have been successfully operated on modified Method 5 trains as with the Battelle Sampler (9) and in recent studies of incinerator emissions (10) in which the version shown in Figure 6 was used. Sufficient quantities of vapors for analysis may frequently be obtained by the simple version of a train previously shown in Figure 3.

Normal care (as specified in Federal Register Method 5) should be taken in both gas and vapor sampling to obtain a representative sample. There is no explicit Level 2 requirement for isokinetic sampling of gaseous species, but samples should either be taken across the cross section of the duct or in a well mixed portion of the stream.

## B. Particulates

Particulates consist of solids and liquid aerosols; both are collected efficiently by appropriate combinations of cyclones and filters. Other special purpose particulate collectors such as electrostatic precipitators have found limited application in the collection of samples for environmental assessment studies related to chemical composition.

There is a wide variety of trains and configurations that can be used to characterize particulate emissions. A complete discussion of these can be found in the EPA reports.

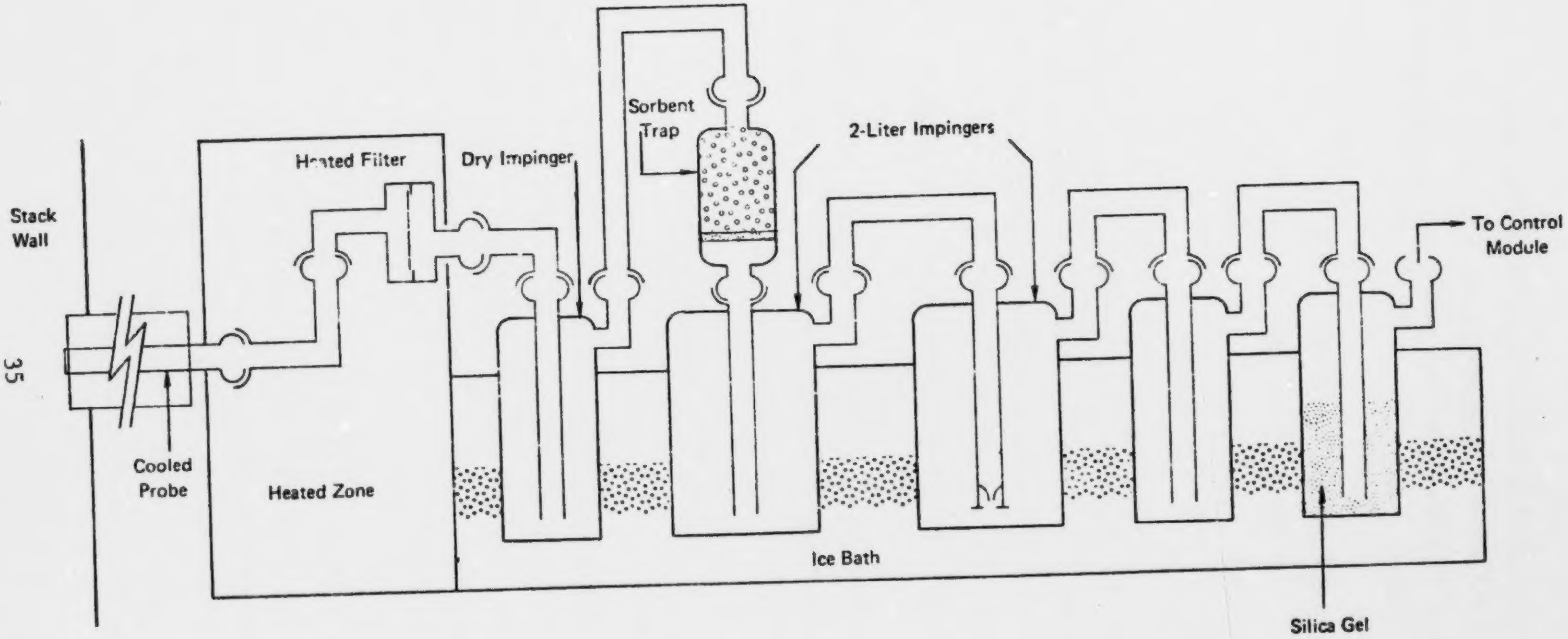

Stack Wall
Cooled Probe
Heated Filter
Heated Zone
Dry Impinger
Sorbent Trap
2-Liter Impingers
Ice Bath
Silica Gel
To Control Module

Figure 6 Method 5: Train Modified for Collection of Organic Vapors

Source: "Destroying Chemical Wastes in Commercial Scale Incinerators". Facility Report No. 5 EPA Contract No. 68-01-2966 TRW Systems Inc., Subcontract No. A82870 DNB-L, Arthur D. Little, Inc. July 1977 p. 14

For chemical characterization studies and to provide samples for biotesting, the SASS train shown in Figure 7 is used for Level 1 studies. The SASS is capable of providing particulate sample in the following size ranges:

| | |
|---|---|
| > 10 μm | cyclone |
| 3 - 10 μm | cyclone |
| 1 - 3 μm | cyclone |
| < 0.5 μm | filter |

The first two and last two size ranges are each combined to yield only two particulate fractions for analysis in Level 1 but can be maintained separately for Level 2 studies. Interest in analysis of each of the size fractions might be related to the relative distribution of the trace metals or pesticides or other species of interest.

For simple quantitative measurement of total particulate emission levels, or if smaller quantities of particulate are required, the Method 5 train (Figure 8) as described in the Federal Register may be adequate.

## C. Liquids/Slurries

The general considerations given in the Level 1 Procedures Manual still pertain for Level 2 sampling of liquid and slurry streams. Stream homogeneity and flow rate are important factors to consider in collecting a representative sample and may be accomplished by a number of well established methods (4).

Grab samples, such as collected in the Level 1 Procedure, may also be used for Level 2 studies. Grab samples will be adequate if the primary Level 2 objective is more complete qualitative chemical or biological characterization than provided in Level 1. However, it is expected that most Level 2 studies will also require better quantitative data and for this purpose proportional sampling should be used.

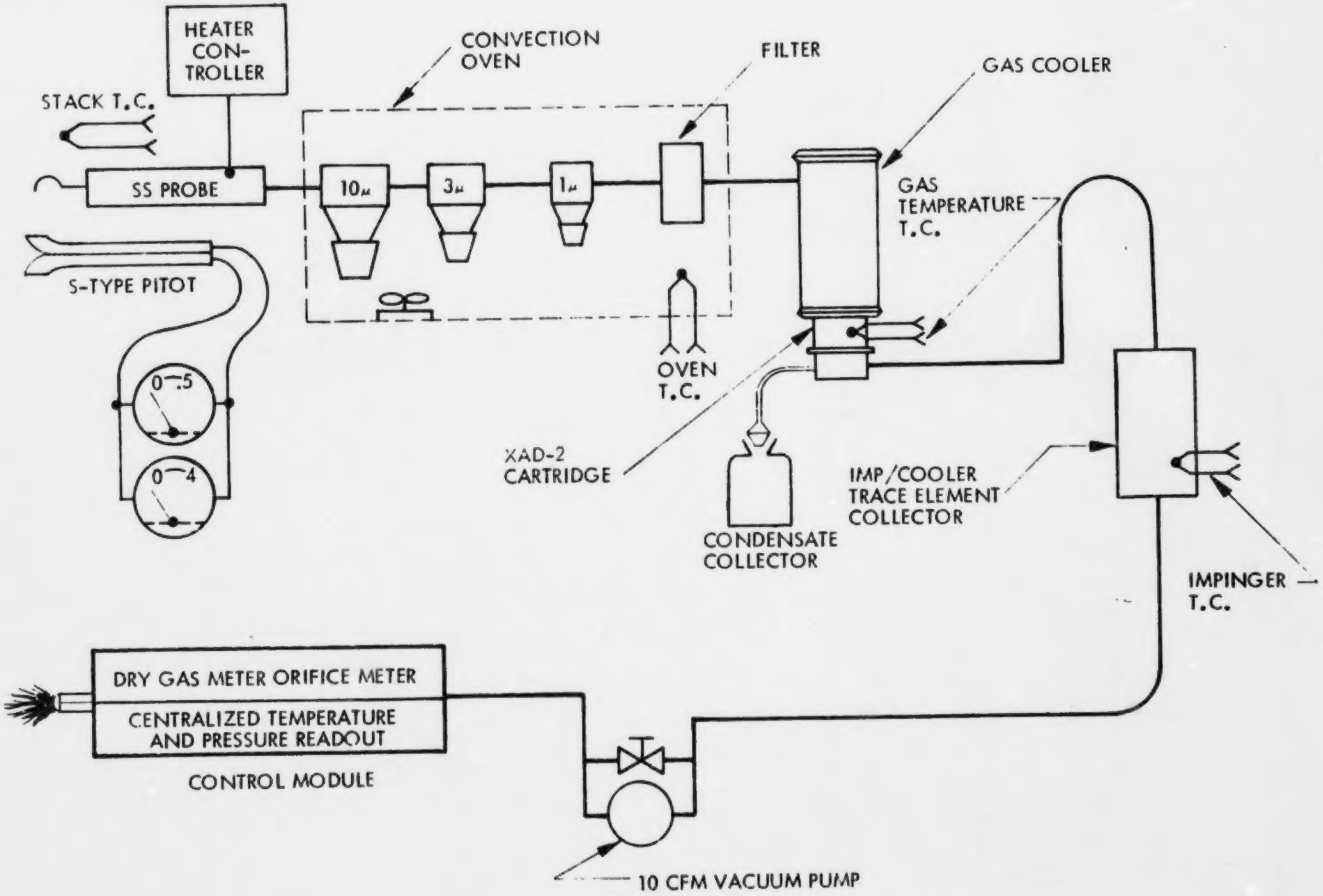

HEATER CON- TROLLER
CONVECTION OVEN
FILTER
GAS COOLER
STACK T.C.
SS PROBE
10μ
3μ
1μ
GAS TEMPERATURE T.C.
S-TYPE PITOT
0—.5
0—4
OVEN T.C.
XAD-2 CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMP

Figure 7 Source Assessment Sampling Schematic

Source: EPA 600/2-76-160a, June 1976 p.30

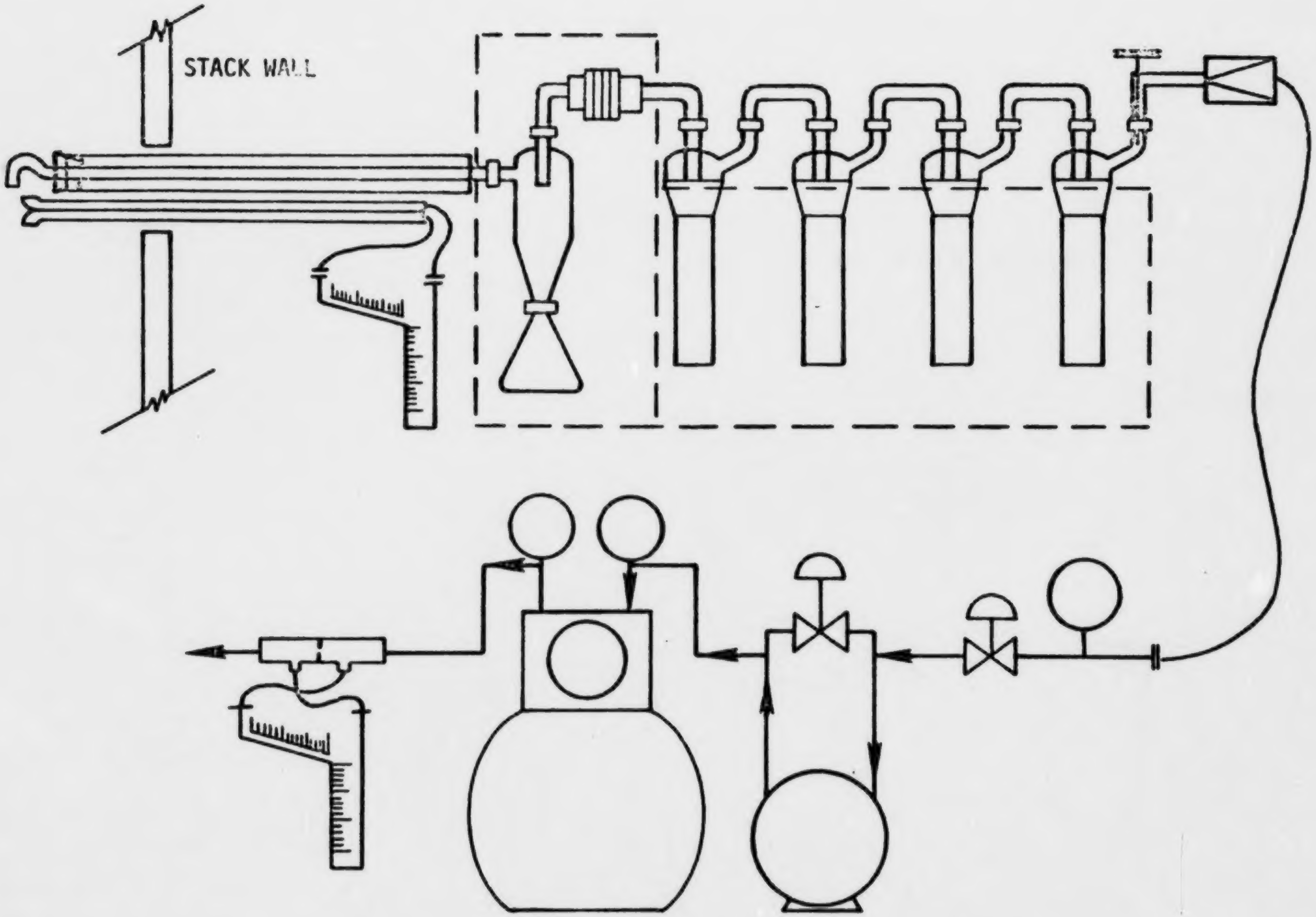


Figure 8 Method 5: Particulate Sampling Train

Source: 40 CFR 60, Appendix A - Government Printing Office, Washington D.C., July 1976

Sampling may be done proportional to either time or flow, and the choice will have to be dictated by the process characteristics and the measurement objectives. It is possible to obtain samplers which provide the substance in a composite or separate sequential mode. Sampling with this type of equipment whould be restricted to streams with low or no visible solids. Slurries should be sampled by grab techniques.

For aqueous streams, grab sampling combined with solvent extraction of organics is a tedious procedure and does not always lead to quantitative extraction. Continuous extraction/concentration techniques used in conjunction with a proportional sampler offer significant promise for obtaining a quantitative time-averaged sample from aqueous liquid streams.

The Carbon Adsorption Method (CAM) has previously been used by EPA in a large number of water and wastewater sampling studies. While the CAM has apparently good extraction efficiency, quantitative recovery of some compounds is poor. Recent studies in the laboratory of EPA (11) and ERDA (12) indicate that XAD-2, XAD-8 and combinations of these resins are good sorbents for the extraction and recovery of ppb-level materials. A program is currently underway on the design of a XAD-2 sampler for use in the field collection of samples.

For high concentrations of organics in water (> 10 ppm) solvent extraction procedures are still recommended. The resins have limited mass capacity and are probably inferior to solvent extraction at high concentration levels.

For Level 2 studies, it is recommended that a separate liquid sample be collected for the analysis of volatile constituents. These volatile species, or "purgeables" have been the subject of recent EPA studies, (13) and this class has been shown to contain many compounds suspected as carcinogens. A number of the compounds on the MEG list would be detected as purgeables in a water sample.

The EPA Cincinnati protocol for purgeables should be adopted for Level 2. This requires collection of a special grab sample sealed with a Teflon faced septum and no head space. The sample should be analyzed by the "purge and trap" procedure of Bellar and Lichtenberg. (14)

When solvent extraction procedures are to be used, it is recommended that several extractions be carried out at each of the two pH extremes. Extraction is suggested at pH 2 and pH 11. Methylene chloride has been found to be effective for many compounds, but other solvents such as diethyl ether may offer advanatages in certain cases. The extraction sequences of -- base/neutrals then acids, or -- acid/neutrals then bases -- have both been evaluated and found successful in certain cases. The former sequence is currently used in the EPA/Cincinnati protocol. The sequence of choice would appear to be affected by problems such as emulsion formation and should therefore be left to the discretion of the individual sampler/analyst and his project officer.

## D. Solids

Level 1 procedures call for the use of a shovel or borer to obtain a sample for biotesting and to determine composition. Level 2 procedures should more systematically address the method of obtaining a representative sample. There are two basic types of solid samples - a bulk sample and a moving sample. Bulk samples include coal piles, sludge disposal areas, etc. Moving samples come from transport systems such as conveyor belts or transfer points. A number of ASTM procedures describe acceptable means of collecting each of these sample types.

For bulk samples, ASTM D346-35, "Standard Method of Sampling Coke for Analysis", describes the basic techniques for shovel, coning and quartering methods and locating sampling points. ASTM D-1799-65, "Sampling Packaged Shipments of Carbon Black", provides a method for bagged or cartoned materials. ASTM C183-71, "Sampling Hydraulic Cement", describes discharge point sampling and a slotted tube sampler for hopper sampling. ASTM D-2013-72, "Preparing Coal for Analysis", describes several mechanical sample dividers and riffles which can be used in preparing a fraction of the sample for analysis.

Moving samples may be collected by several procedures. A "stop belt" method involves stopping periodically and removing a standardized portion of the stream, taking care to obtain a complete cross section, since settling will occur. A cutter device, as described in ASTM D 2234-72, removes a portion of the stream by a traverse at a uniform speed. Samples from discharge points may be collected by moving a pan across the entire cross section of the discharge.

## E. Fugitive Emissions

Fugitive emissions are all those emissions discharged to the environment by a source other than a well-characterized stack or stream. They may include particulate, vapor, gas and water samples or species. Fugitive emissions can be considered to be dilute source samples at ambient conditions. The dilution factor requires special consideration in sample volumes required for collection. The fact that fugitive emission species are defined only as being present in the ambient environment poses special sampling strategy problems for sampler choice and location.

The general characteristics of fugitive emissions and sampling methodology have been described in recent IERL-RTP reports. (7a, b, c.)

Airborne fugitive emissions may generally be described in terms of:

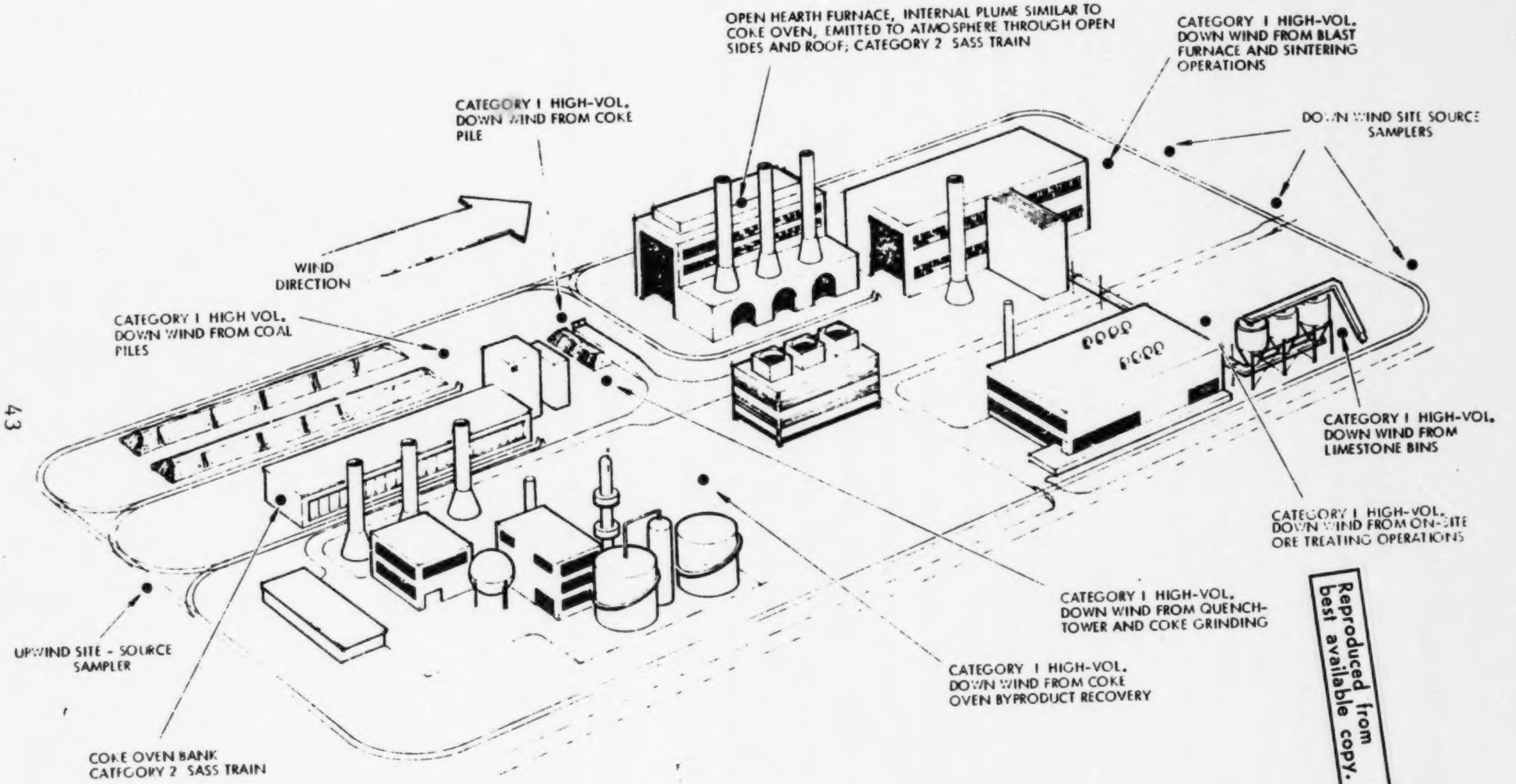
Site Source
Specific Source: Category 1
Specific Source: Category 2

Several examples of these are described in a worst case site description in Figure IV-8. A "site source" is a general emission contributed to by many individual sources. Sampling such a source requires an upwind/downwind strategy. Some specific diffuse sources, Category 1, can be sampled by placing a sampler directly downwind if it has minimum confusion by other sources. Other specific sources, Category 2, are less diffuse, such as hearth or coke oven vents, and may be sampled using point source sampling methods.

Particulate samples from site sources and Category 1 specific sources may be sampled using a Hi-Vol sampler. If size fractionation is desired, a Hi-Vol impactor stage may be added. For Category 2 specific sources, the same choices for stack methods described in Section IV.B. are applicable. Primary emphasis in a level 2 study may be on better quantitative data which will required collecting a large number of samples with associated meteorological and source data.

By operating at about 50 cfm the Hi-Vol sampler is generally capable of collecting sufficient fugitive particulate sample for study (chemical analysis). There is no analagous equipment or method for sampling fugitive gases and vapors. The ambient/fugitive concentrations are 100 - 10,000 times lower than source levels, but the currently available methodology will not allow flow rate scaling to collect large quantities. Although there has been only limited testing, it is believed that the general bag and sorbent (Tenax GC) procedures described in Section IV A for source levels will provide sufficient sample for chemical analysis studies of fugitive vapors and gases. However, use of these methods for this purpose requires further careful validation.

The same procedures described for Level 1 fugitive water sampling are recommended for Level 2 studies, if required.


OPEN HEARTH FURNACE, INTERNAL PLUME SIMILAR TO COKE OVEN, EMITTED TO ATMOSPHERE THROUGH OPEN SIDES AND ROOF; CATEGORY 2 SASS TRAIN
CATEGORY I HIGH-VOL. DOWN WIND FROM BLAST FURNACE AND SINTERING OPERATIONS
CATEGORY I HIGH-VOL. DOWN WIND FROM COKE PILE
DOWN WIND SITE SOURCE SAMPLERS
WIND DIRECTION
CATEGORY I HIGH VOL. DOWN WIND FROM COAL PILES
CATEGORY I HIGH-VOL. DOWN WIND FROM LIMESTONE BINS
CATEGORY I HIGH-VOL. DOWN WIND FROM ON-SITE ORE TREATING OPERATIONS
CATEGORY I HIGH-VOL. DOWN WIND FROM QUENCH-TOWER AND COKE GRINDING
UPWIND SITE - SOURCE SAMPLER
CATEGORY I HIGH-VOL. DOWN WIND FROM COKE OVEN BYPRODUCT RECOVERY
COKE OVEN BANK CATEGORY 2 SASS TRAIN

Reproduced from best available copy.

Figure 9 Decision Example for "Worst Case" Site

Source: EPA 600/2-76-160a, June 1976 p.51

## F. Reactive Compounds

There are many specific compounds which are reactive and would not persist in a general sampling and analysis scheme long enough for quantitative and possibly even qualitative determination. For example, examination of the MEG list of organic compounds (8) shows several species or categories which will need special attention if the need should arise to determine them. (See Table 3).

For some compounds, there are relatively straightforward solutions. For instance, the low FID response of the alkyl halides can be overcome by using an ECD detector. The reactive mercaptans can be analyzed by GC on-site (as in Level I). However, the compounds which pose a problem because of very high reactivity represent a more difficult case. Specific methods will have to be used for each of these cases. In some cases, as for the aldehydes, methodology exists in the form of a specific bisulfite collection followed by iodometric titration or GC analysis. Some other species, such as the dienes, will require development of special sampling and analysis methods. It may be possible to modify a colorimetric procedure to measure the level of azo compounds and hydrazines.

Each of the compounds or categories listed in Table 3 (and perhaps others) represents a special case which must be handled on an individual basis.

## TABLE 4

### Problematic Organic Compound Categories

| Category | Problem |
|---|---|
| Alkynes | reactive |
| Haloforms | low response to F.I.D. |
| Halogenated Dienes | reactive |
| Halogenated Ethers (some) | reactive |
| Aldehydes | reactive |
| Methyl Methacrylate | reactive |
| Acrylonitrile | reactive |
| Azo compounds, Hydrazine and derivatives | reactive |
| Mercaptans | reactive (on-site GC) |
| Dicyclopentadiene | reactive |

# V. ANALYSIS METHODS

## A. Liquid Chromatography

In Level 2 organic analysis, as in Level 1, it will usually be necessary or desirable to perform some sample fractionation prior to analysis. One approach to sample fractionation is liquid column chromatography (LC) on media such as silica gel, alumina, or Florisil. An LC separation on silica gel is often useful as a method for separating a sample into a small number (i.e., 4-8) of fractions prior to bioassay or chemical characterization. An eight-fraction scheme of this type is used in Level 1 organic analysis and in some cases it may be possible to use those same eight fractions for further, Level 2 analysis. In the more general case, in which discrete Level 2 samples have been collected, alternative fractionation procedures are likely to be attractive.

A number of different LC schemes will be used in Level 2, depending on which categories of compounds are of concern. Furthermore, since Level 2 analysis will ordinarily be directed towards only one or a few specific categories of compounds identified in Level 1, a simple two- or four-fraction LC separation may suffice. One example is shown in Figure 10 for Level 2 analysis of phenols.

Other LC procedures that are of value in Level 2 organic analysis are separations on alumina or Florisil to remove interferences in the analysis of selected substances. An example, shown in Figure 11, is the Florisil column pre-cleaning procedure used to remove interfering substances prior to analysis of polychlorinated biphenyls (PCB's) in industrial effluents (15). Another example of possible application of LC in Level 2 organic analysis is shown schematically in Figure V-3. In this example, a silica gel LC procedure to isolate aromatics is followed by an alumina LC procedure to separate polynuclear aromatics into classes by ring number.

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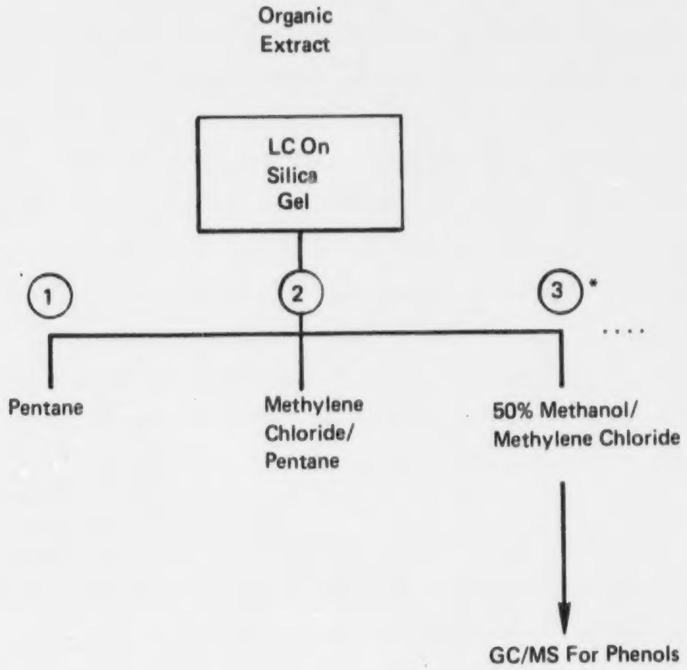

Organic Extract
LC On Silica Gel
①
②
③*
....
Pentane
Methylene Chloride/ Pentane
50% Methanol/ Methylene Chloride
GC/MS For Phenols

*Or Fraction 6 From Level 1 LC Scheme

FIGURE 10. DIRECTED LEVEL 2 LC SCHEME FOR ANALYSIS OF PHENOLS

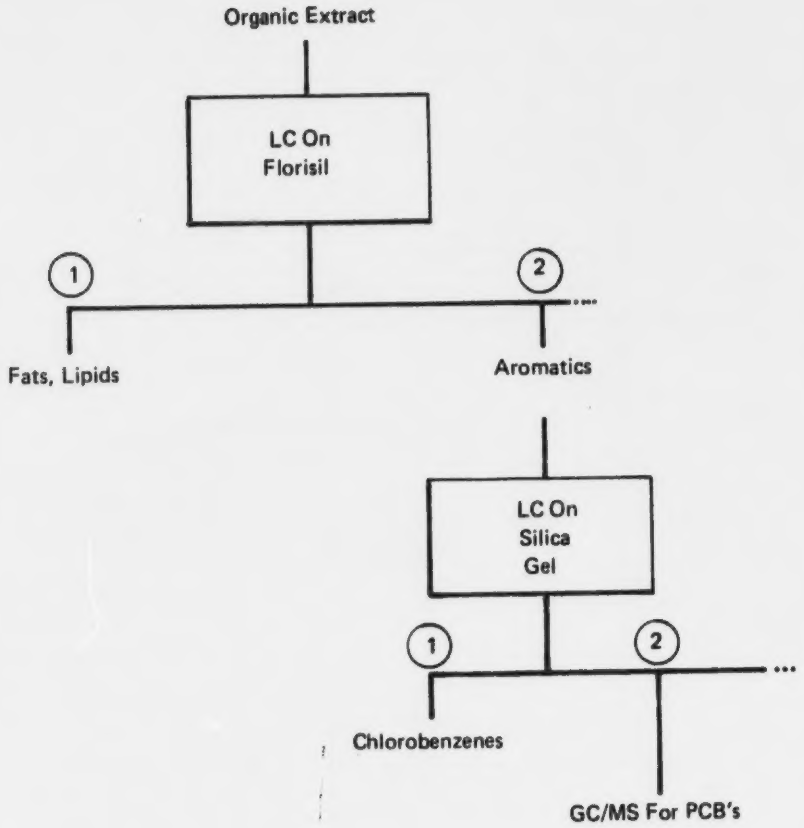
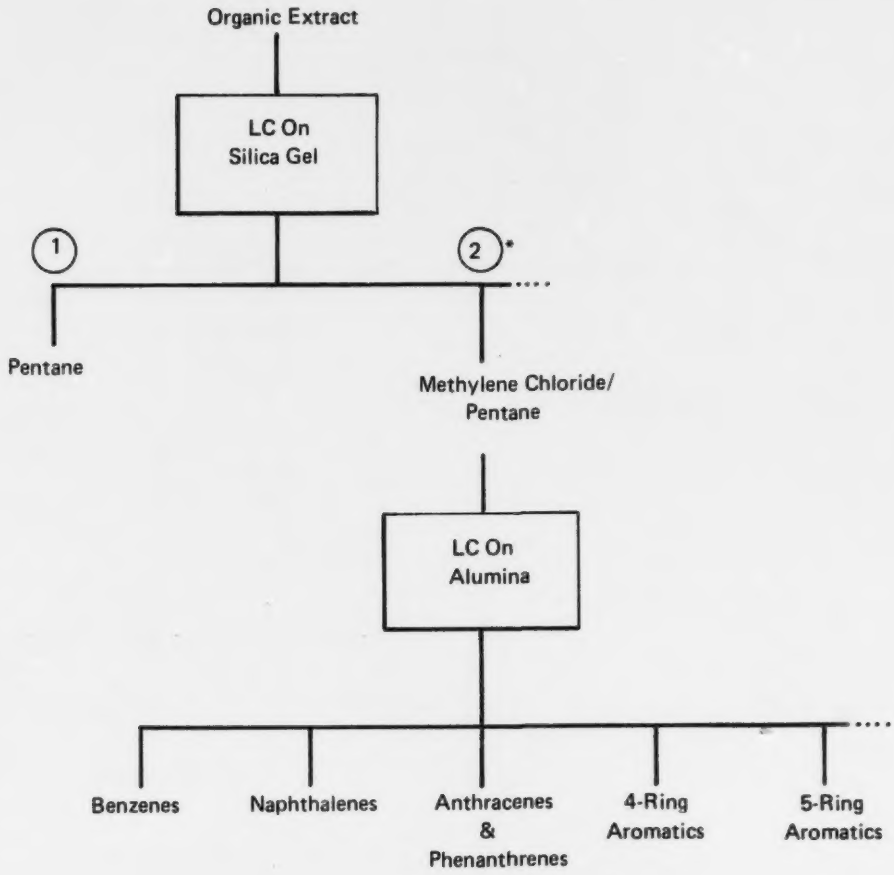

Organic Extract
LC On Florisil
①
②
Fats, Lipids
Aromatics
LC On Silica Gel
①
②
Chlorobenzenes
GC/MS For PCB's

FIGURE 11. DIRECTED LEVEL 2 LC SCHEME FOR ANALYSIS OF POLYCHLORINATED BIPHENYLS



Organic Extract
LC On Silica Gel
①
②*
Pentane
Methylene Chloride/ Pentane
LC On Alumina
Benzenes
Naphthalenes
Anthracenes & Phenanthrenes
4-Ring Aromatics
5-Ring Aromatics

*Or combined Level I LC Fractions 2, 3 and 4.

FIGURE 12. DIRECTED LEVEL 2 LC SCHEME FOR ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS

## B. High Performance Liquid Chromatography (HPLC)

HPLC is a separation technique with applications in quantification, isolation and identification. HPLC is differentiated from other LC methods by high speed, high sensitivity and high resolution comparable to that of gas chromatography. These improvements have been achieved by columns using microparticle packings with small diameter (5-50 micrometers) and high surface area (approximately 300 $m^2/g$ particles. Separations may be achieved by differences in molecular size, number or type of functional groups, steric configuration, polarity, etc.

### 1. Detectors

The two most commonly used methods of detection of sample components in HPLC effluents are ultraviolet (UV) absorbance detectors and refractive index (RI) detectors. Features of these two types of detectors are summarized in Table 4. High sensitivity and specificity are achievable using a UV detector at fixed (e.g., 254 nm) or variable (200-800 nm) wavelength. Lower limits of detection in the nanogram range have been reported for strongly absorbing sample species (i.e., molar absorbtivity $\gtrsim$ 14,000. Table 5 presents some molecular absorbtivity data to illustrate the range of detection limits that can be expected for the UV detector. The differential refractometer detector has lower sensitivity and less specificity than the UV detector. The RI detector responds to essentially all sample components and is a potential "universal" detector for HPLC, but lower limits of detection are in the microgram range. Furthermore, generality of the RI detector response requires matching of solvent system refractive indices during gradient elution HPLC; this is difficult to achieve in lab practice. Other types of HPLC detectors, such as the moving wire flame ionization detector and the fluorescence detector, do not appear to offer any special advantages for Level 2 organic analysis compared to the UV and RI detectors. The fluorescence detector might be applied in some specific cases, such as analysis of polynuclear aromatic hydrocarbons.

TABLE 5

## Comparative Specifications of HPLC Detectors

| | UV | RI |
|---|---|---|
| Range of Application | Selective | Universal |
| Destructive or Non-destructive | Nondestructive | Nondestructive |
| Gradient Compatible | Yes | -- |
| Detectability | | |
| Min. Physical Change | $2 \times 10^{-4}$ Abs. | $1 \times 10^{-7}$ RI units |
| Minimum Concentration | $4 \times 10^{-9}$ g/mL | $7 \times 10^{-7}$ g/mL |
| Minimum Det. Sample | $\sim 2 \times 10^{-11}$ g/sec | $\sim 3 \times 10^{-9}$ g/sec |
| Linear Range | 3000 | 3000 |
| Short Term Reproducibility | Less than 1% deviation | Less than 1% deviation |
| Peak Shape | Positive only | Positive or Negative |
| Peak Spreading | | |
| Nom. Response Time | 1 second | 1 second |
| Cell Void Volume | 8 microliters | 6 microliters |
| Experimental Upper Limit | 46 microliters | 20 microliters |
| Flow Sensitivity (b.l. shift 0-90 mL/hr) | 12% f.s. | ~25% f.s. |

Source: Basic Liquid Chromatography, Varian Instrument Company

TABLE 6

## Electronic Absorption Bands for Representative Chromophores

| Chromophore | System | λ Max | ε Max | λ Max | ε Max | λ Max | ε Max |
|---|---|---|---|---|---|---|---|
| Ether | -O- | 185 | 1000 | | | | |
| Thioether | -S- | 194 | 4600 | 215 | 1,600 | | |
| Amine | $-NH_2$ | 195 | 2800 | | | | |
| Thiol | -SH | 195 | 1400 | | | | |
| Disulfide | -S-S- | 194 | 5500 | 255 | 400 | | |
| Bromide | -Br | 208 | 300 | | | | |
| Iodine | -I | 260 | 400 | | | | |
| Nitrile | $-C\equiv N$ | 160 | - | | | | |
| Acetylide | $-C\equiv C-$ | 175-180 | 6000 | | | | |
| Sulfone | $-SO_2-$ | 180 | - | | | | |
| Oxime | -NOH | 190 | 5000 | | | | |
| Azido | >C=N- | 190 | 5000 | | | | |
| Ethylene | $-C\equiv C-$ | 190 | 8000 | | | | |
| Ketone | >C=O | 195 | 1000 | 270-285 | 18-30 | | |
| Thioketone | >C=S | 205 | strong | | | | |
| Esters | -COOR | 205 | 50 | | | | |
| Aldehyde | -CHO | 210 | strong | 280-300 | 11-18 | | |
| Carboxyl | -COOH | 200-210 | 50-70 | | | | |
| Sulfoxide | >S→O | 210 | 1500 | | | | |
| Nitro | $-NO_2$ | 210 | strong | | | | |
| Nitrite | -ONO | 220-230 | 1000-2000 | 300-400 | 10 | | |
| Azo | -N=N- | 285-400 | 3-25 | | | | |
| Nitroso | -N=O | 302 | 100 | | | | |
| Nitrite | $-ONO_2$ | 270<br>(shoulder) | 12 | | | | |
| | $-(C=C)_2-$<br>(acyclic) | 210-230 | 21,000 | | | | |
| | $-(C=C)_3-$ | 260 | 35,000 | | | | |
| | $-(C=C)_4-$ | 300 | 52,000 | | | | |
| | $-(C=C)_5$ | 330 | 118,000 | | | | |
| | $-(C=C)_2-$<br>(alicyclic) | 230-260 | 3000-8000 | | | | |
| | $C=C-C\equiv C$ | 219 | 6,500 | | | | |
| | C=C-C=N | 220 | 23,000 | | | | |
| | C=C-C=O | 210-250 | 10,000-20,000 | | | 300-350 | weak |
| | $C=C-NO_2$ | 229 | 9,500 | | | | |
| Benzene | | 184 | 46,700 | 202 | 6,900 | 255 | 170 |
| Diphenyl | | | | 246 | 20,000 | | |
| Naphthalene | | 220 | 112,000 | 275 | 5,600 | 312 | 175 |
| Anthracene | | 252 | 199,000 | 375 | 7,900 | | |
| Pyridine | | 174 | 80,000 | 195 | 6,000 | 251 | 1,700 |
| Quinoline | | 227 | 37,000 | 270 | 3,600 | 314 | 2,750 |
| Isoquinoline | | 218 | 80,000 | 266 | 4,000 | 317 | 3,500 |

Source: Basic Liquid Chromatography, Varian Instrument Company

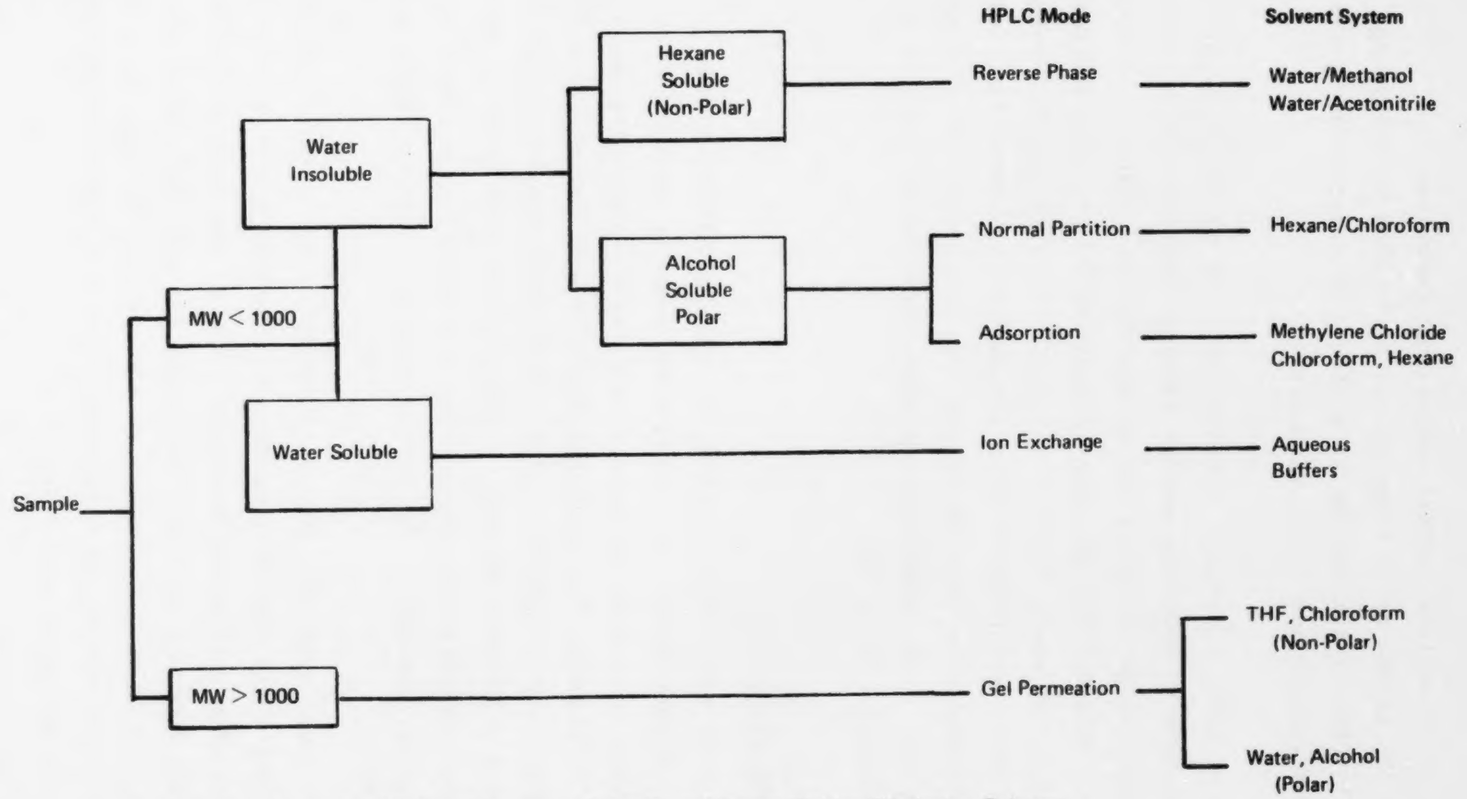
An HPLC-MS combination might be of interest in some Level 2 applications. However, these systems are not in common use because of the formidable problems in designing an interface to remove carrier (solvent) prior to MS analysis. Similarly, the FTIR detector offers great promise when and if it becomes fully developed for this application.

HPLC methods are likely to be used in two different modes in Level 2 organic analysis. First, some HPLC separations by Gel Permeation, normal, or reverse phase chromatography are useful ways of achieving a preliminary coarse fractionation of the sample according to molecular weight range and polarity. Secondly, some normal or reverse phase chromatographic procedures may be selected as the quantitative analytical finish for sample components that have high molecular weight, poor thermal stability, and/or high polarity. A guide to selection of an analytical HPLC method is summarized in Figure 13. In practice, of course, the use of such a guide would require that determination be made at each decision point to provide information required for the choice. The types of HPLC separations most useful in Level 2 organic analysis are discussed briefly below.

### 2. Gel Permeation Chromatography

This technique is based on separation by molecular size, which is closely related to molecular weight. Large molecules may be excluded from some or all of the pores in the column packing material, due to their hydrodynamic volume in solution. Therefore, large molecules elute from the column before smaller molecules which permeate the pores. Columns are available in a variety of nominal pore sizes, and a number of columns are usually used in series to ensure adequate resolution.

Column packings used with non-aqueous mobile phases (for example, tetrahydrofuran, toluene, dimethylformamide and methylene chloride) include polystyrene (e.g., Styragel®), spherical silica (e.g., Porasil®) and irregularly shaped silica (e.g., Merkogel® Si). Packings suitable for use in aqueous GPC include Dextran gels (e.g., Sephadex®) and controlled pore-size glass (e.g., CPC®).


HPLC Mode
Solvent System
Sample
MW < 1000
MW > 1000
Water Insoluble
Water Soluble
Hexane Soluble (Non-Polar)
Alcohol Soluble Polar
Reverse Phase
Water/Methanol
Water/Acetonitrile
Normal Partition
Hexane/Chloroform
Adsorption
Methylene Chloride
Chloroform, Hexane
Ion Exchange
Aqueous Buffers
Gel Permeation
THF, Chloroform (Non-Polar)
Water, Alcohol (Polar)

Adapted from Literature of DuPont Instruments, Scientific and Process Division Wilmington, Delaware

FIGURE 13. GUIDE TO SELECTION OF HPLC ANALYTICAL PROCEDURES

GPC may be used to achieve initial sample fractionations on a fairly large scale, since 150 to 200 mg of material may be handled by μ-Styragel columns. Even higher loading capacities can be achieved by using larger particle sizes (macro-Styragel) and column diameters.

For purposes of Level 2 organic analysis, GPC will probably be most useful as a technique to separate samples into two molecular size ranges, with a molecular weight of about 500 as the dividing point. The species with molecular weight < 500 can then be analyzed by gas chromatography or GC/MS, although some small and very polar or thermally unstable molecules (amino acids, etc.) may require derivativization or alternative treatment. The sample components in the >500 mw cut will require analysis by methods not involving GC. These might include mass spectrometry (LRMS or HRMS) or Fourier transform IR or NMR.

### 3. Reverse Phase HPLC

This technique is based on separation by polarity differences in the mobile phase vs. stationary phase. The stationary phase is prepared by using long-chain alkyl silylating reagents to produce a hydrophobic layer on a silica solid substrate. Non-polar solutes have a higher affinity for the stationary phase than do polar solutes. The mobile phase is generally programmed in a continuous gradient elution scheme from polar to non-polar solvents. Water/methanol and water/acetonitrile are binary solvent systems frequently employed. In reverse phase HPLC, polar sample components elute first.

In Level 2 organic analysis, reverse phase HPLC may be applied to low molecular weight range sample components to separate the polar materials, which would require derivative formation prior to gas chromatographic or GC/MS analysis, from the non-polar materials suitable for direct gas chromatography or GC/MS. Reverse phase HPLC is also an attractive possibility for ultimate quantitative analysis of some classes of compounds, such as phenols and carboxylic acids.

### 4. Normal Phase HPLC

This technique, like reverse phase HPLC, is based on separation by polarity. In normal phase separations, the stationary phase is more polar than the mobile phase. Gradient elution systems from non-polar to polar solvents are used, and non-polar solutes elute first. In Level 2 organic analysis, normal phase HPLC may be used as a quantitative analytical finish for some classes of compounds. The choice between normal and reverse phase systems for this purpose would be based on several considerations.:

(1) Quantity of solute to be isolated for qualitative identification by NMR, IR, etc.
(2) Solute class solubility in the mobile phase.
(3) Column capacity for solutes in general.
(4) Ease of solvent removal after HPLC.

The first point is amply illustrated by considering the separation of polycyclic aromatic hydrocarbons. Excellent separations between these solutes is accomplished using $H_2O$/MeOH isocratic and gradient mixtures as solvents. With these solvent systems and a $C_{18}$-silylated silica support, even the isomeric pair of phenanthrene and anthracene can be partially separated. However, despite the excellent thermodynamic selectivity of this HPLC system, it is limited in the quantity of solute which can be chromatographed. This is in part due to the lower capacity of reverse phase packings, the normal loss in resolution with sample overload, but primarily due to the solubility limit of the hydrocarbon moiety in polar solvents. Using a hydrocarbon solvent in conjunction with a silica support (normal phase system) allows larger quantities of this particular class to be isolated (larger capacity of support, higher solubility, etc.) although the resolution is diminished. It should be noted that sample solubility in the mobile phase is of prime consideration in preparative chromatography, particularly when mild gradients (water to methanol, n-hexane to methylene chloride) are used in reverse or normal phase systems.

If HPLC is to be used to isolate large quantities of material, the column capacity becomes a factor. For example, semi-preparative reverse phase columns have a typical capacity of 5 mg while a micro-particulate silica gel for normal phase LC has a capacity of 1000 mg. It is therefore not always possible to simply scale-up an analytical reverse phase HPLC separation to achieve a preparative procedure.

It should also be noted that subsequent analytical procedures to be applied to HPLC fractions will possibly necessitate the removal of solvent from the collected fractions. Water/methanol eluents can be more difficult to remove than a volatile hydrocarbon and may result in the loss of some of the analyte. From this point of view, normal phase would seem to offer some advantages.

## C. Thermal Gravimetric Analysis (TGA)

The techniques which are used for the ultimate qualititative and quantitative Level 2 analysis will depend on the volatility of the sample components. Analytical procedures based on gas chromatography (GC), including GC/MS, are suitable for volatile components. Sample components that are non-volatile (because of high polarity and/or high molecular weight) must be separated and analyzed by other techniques. Thermal Gravimetric Analysis (TGA) is a rapid instrumental method for quantitatively determining the volatility of a sample as a function of temperature.

In a TGA analysis, the weight of a small sample (1-10 mg) is continuously recorded as a function of time (isothermal operation) or temperature (temperature programmed operation). The water content in mixtures, for example, may be determined by TGA due to the well-defined weight loss at its boiling point. In addition, isothermal TGA can be used to determine residue on ignition on a micro scale by isothermal operation at high temperature. For sample characterization studies, temperature programmed operation is more normally used. The sample atmosphere (nitrogen, air, etc.) may be controlled to aid in the study, for instance, of decomposition of non-volatile samples.

An example of the applicability of TGA to Level 2 organic analysis would be the determination of whether the "aromatic" material indicated as present in a source by Level 1 analysis is more suited to separation and analysis by GC/MS or by HPLC.

## D. Gas Chromatography (GC)

Gas chromatography is a very powerful tool for separation of complex mixtures of organics with appreciable volatility. GC is also an exceedingly valuable technique for quantitative analysis of sample components. However, qualitative analysis by GC is limited to inferences drawn from retention times of individual peaks and known detector selectivities. (The combination of mass spectrometric detection with GC to give qualitative data is discussed in a separate section).

### 1. Detectors

A considerable variety of detection principles have been utilized for gas chromatography purposes. Of the detectors available, there are three which are potentially of interest in Level 2 organic analysis.

The flame ionization detector (FID) is the most versatile general purpose device. The FID responds to any substance that will burn in the air/hydrogen flame to produce ions. Most organics, except for highly halogenated species, give strong FID responses. The lower limit of detection for organic species is on the order of one nanogram per microliter (ppm) of injected solution, and the dynamic range of the detector spans four or more orders of magnitude.

The electron capture detector (ECD) is specific for species that contain electronegative atoms or groups--halogens, phosphorus, sulfur, and nitrogroups. The high selectivity of the ECD has been used to good advantage in analyses of pesticides and polychlorinated biphenyls (PCB's). The lower limit of detection is as much as 1000 times lower than that of the FID, but the dynamic range is generally smaller. The magnitude of the ECD response is sensitive to analyte structure, as well as to concentrations, since different species have different electron capture cross sections. The detector response is also temperature dependent, so that an ECD cannot usefully be employed in temperature programmed GC. All of these factors combine to support the conclusion that GC/ECD is not a technique with wide applicability in Level 2 organic analysis, but one which may be used for some specific categories of analytes.

The flame photometric detector (FPD) is specific for species that contain sulfur or phosphorus. Its specificity, detection limits, and sensitivity are comparable to those of the ECD, although a completely different principle of detection is involved. When operated in the sulfur mode, the FPD response is logarithmic, rather than linear, with concentration. The FPD may be utilized in Level 2 organic analysis of organophosphorus pesticides and some sulfur species (including on-site analysis of reactive sulfur gases, as in Level 1).

### 2. Columns

The number of potential choices of column type for Level 2 organic analysis is staggering. Columns may be packed, support coated open tubular (Scot) or wall-coated capillary column of stainless steel, glass, or Teflon. An enormous range of stationary phases is available, including porous polymers and liquids coated onto solid substrates. Highly specialized columns include the polyphenylether/phosphoric acid on Teflon® matrix used for sulfur gases and the recent nematic phase liquid crystal packings used to achieve resolution of isomeric polynuclear aromatic hydrocarbons. These types of columns may be required in special Level 2 situations.

However, it appears that a set of five or six GC columns can be specified that will cover most Level 2 analysis requirements and would maximize comparability of data acquired in different EA programs. A suggested set of columns for general purpose Level 2 work is the following:

- For volatiles - Porapak Q (2 mm x 2 m stainless steel). This porous polymer column can separate hydrocarbons boiling between -161°C and 68°C in a single temperature programmed run. Fairly high resolution within a narrower boiling range can be achieved by isothermal operation.
- For moderate volatility, non-polar species - Methyl Phenyl Silicone (SP 2250 or OV-17). (3% on Chromosorb WHP or equivilent, 2 mm x 2 m stainless steel.) This stationary phase separates analytes primarily on the basis of volatility (boiling point) and can be used at temperatures up to 375°C. The liquid phase is a 50% phenyl silicone.
- For high boiling, non-polar species - Dexsil 400 (3% on Chromosorb WHP or equivalent, 2 mm x 2 m stainless steel). Dexsil 400 is a carborane-methyl phenyl silicone that is stable at temperatures up to 500°C. Like OV-17, Dexsil 400 is basically a boiling point column. It is useful for analyzing species such as the polynuclear aromatics. It does not function well much below 80°C.
- For moderately volatile and moderately polar species - Modified Carbowax 20M (SP 1000) (10% on Chromosorb W, 2 mm x 2 m glass or stainless steel). Polyethylene glycol (Carbowax 20M) modified with a terephthalalic acid, as in SP-1000, is a liquid phase suitable for analysis of a variety of moderately polar species including ethers, carbonyl compounds and alcohols. It can be used at temperatures up to 275°C.
- For moderately volatile and highly polar species - Tenax GC (2 mm x 2 m, glass). This porous polymer is a recommended medium for general GC analysis of phenols and carboxylic acids. It has high thermal stability up to 375°C. (Note that in Level 2 organic analysis, very polar analytes will be analyzed by HPLC, rather than GC, in most cases.)

### 3. Gas Chromatographic Conditions

Details of gas chromatographic conditions, such as carrier gas and temperature regimes, will vary depending upon the compound categories of interest. In general, temperature programming will probably be required for Level 2 analyses.

## E. Gas Chromatography/Mass Spectrometry (GC/MS/DS)*

The combination of gas chromatographic (GC) separation methods with mass spectrometric (MS) detection coupled with an automated data system (DS) is an extremely powerful tool for analysis of organic compounds. The GC/MS technique differs from other GC procedures discussed earlier in that GC/MS can provide specific qualitative information as well as quantitative data about sample components.

### 1. Detector

The detector in GC/MS is a dedicated low resolution mass spectrometer. This has the unique benefit of being both highly compound specific and having substantially uniform response to all components that are sufficiently volatile to pass through the gas chromatograph. Furthermore, under normally favorable circumstances, the MS/DS can discriminate among and often provide discrete quantitative data for two or more components that elute simultaneously from the GC. Lower limits of detection for conventional (non-capillary) column GC are typically 30-100 ng/µl of solution injected, and lower for capillary column GC.

The GC/MS combination has available a range of operating conditions that significantly affect the performance of the system. The operating parameters chosen must be appropriate to the objectives of each particular analysis if the optimum results are to be obtained.

The most significant choices concern the mode of ionization, and the format for mass scanning. Two classes of ionization mode are generally available: electron impact (EI) and chemical ionization (CI). EI provides energy in excess of that required for simple ionization, resulting in considerable fragmentation of the parent molecule. This fragmentation provides structural information and a characteristic signature for a given compound or compound class. Since reference spectra generally available are of the EI type, this ionization mode facilitates direct matching of spectra for species identification. For some compound types the fragmentation is so extensive that the parent ion is difficult or impossible to detect, making specific identification impossible. CI provides a much gentler mode of ionization, yielding fewer fragment ions and substantially larger parent ions. It is the method of choice for those classes which give no EI parent ion, such as the higher mass alcohols, or for those which give very small parent ions with less fragmentation; however, less structural information is provided, although some is available and may be of a unique type. Reactions with the CI reagent gas complicate the spectrum somewhat.

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* In this discussion, the term GC/MS is intended to imply also the existence of an automated data handling system which is a virtual necessity for Level 2 organic analysis.

A range of adjustments is available for both EI and CI, offering some intergradation of features. By varying the reagent gas composition, CI spectra can be made to approach the fragmentation pattern obtained in EI; reducing the electron beam energy in EI can simplify the fragmentation pattern of that mode. EI is somewhat more universal in application, as it provides a more consistent sensitivity from species to species, but CI can provide unique information that is sometimes necessary for identification. Both techniques can be used for the same material provided sufficient sample and time are available for multiple analyses.

The adjustable parameters in selection of a GC/MS mass scanning format are the range of the scan (or number of masses monitored) and the dwell time on each ion. These must combine to give a fast enough scan to yield several scans per GC peak; each complete scan must therefore last a few seconds at most. One alternative is to scan the entire (i.e., m/e 12 to m/e 600) mass spectrum of material eluting from the column at a frequency of about one scan every three seconds. However, the option of scanning the entire available mass range is normally chosen only if absolutely nothing is known about the sample. In virtually all Level 2 analyses, sufficient information will be available about the sample composition and/or the components of particular interest to allow one to scan a more limited mass range. For example, the mass scan could be limited to the range of m/e 100 to 300 if polynuclear aromatic hydrocarbons were the only compounds of concern. If a specific GC/MS analysis for PCB's was desired, a few selected clusters of masses corresponding to the di-, tri-, tetra-, etc., chlorobiphenyls could be monitored instead of scanning a continuous wide mass range. The extreme case of limited mass scanning would be to monitor a single ion continuously, if only one compound were of interest. Reducing the range of the mass scan allows an appreciably longer dwell time on each ion and this is used to improve the signal to noise ratio. A limited mass scan also enhances sensitivity by reducing background. The background elimination can also be effected in the data processing phase, but the dwell time for each ion is a real time parameter which is fixed during data acquisition.

The improvement in effective sensitivity can be as much as three orders of magnitude between the extremes of a complete mass scan and single ion monitoring. Limited mass range scanning of selected ions or clusters can approach the sensitivity of single ion monitoring.

The selection of the appropriate mass scan range will depend on the objectives of each particular Level 2 analysis. The presentation of the data accumulated in the GC/MS scans can also be varied according to the requirements of the analysis. One can print out a "reconstructed gas chromatogram" in which the sum of ions of all mass numbers for each scan is plotted versus mass spectrum scan number (a measure of retention time). A second alternative is to plot the data in the form of "mass chromatograms", in which only the abundance of selected ions, with m/e values corresponding to specific sample components, is considered. The mass chromatogram approach is especially useful for quantitative analysis of known components. In all cases, however, the quantitative data obtained from the selected ion mass chromatogram(s) must be supported by qualitative identification of the component producing the chromatographic peak(s). The confirmation of identity should be achieved by performing an initial GC/MS run using a broad mass range scan (i.e., m/e 40 through the molecular weight of the component) and directing the data system to print out the mass spectrum of the scan(s) corresponding to the GC peak in question.

In interpreting the GC/MS results it is also important to consider retention time data as well as the mass spectra. If the MS data appear to show benzpyrene eluting ahead of phenanthrene from a Dexsil 400 column, it is reasonably certain that at least one of these compound assignments is incorrect. If reference samples of known components are available, absolute, as well as relative, retention times (RRT) can be used in interpreting GC/MS data. It is frequently useful to use internal standards, such as p,p'-DDE, for the purpose of establishing RRT's.

### 2. Columns

The discussion of gas chromatographic columns, which was presented above in the discussion of GC (Section D.2), holds equally well for GC/MS. The same five basic columns--Porapak Q, SP-2250 or OV-17, Dexsil 400, SP-1000, and Tenax GC--are expected to be used for the bulk of Level 2 GC/MS work.

## F. Mass Spectrometry (LRMS and HRMS)

There are two principal mass spectrometric techniques, in addition to GC/MS discussed above, that are applicable to Level 2 organic analysis. These are low resolution mass spectroscopy (LRMS) and high resolution mass spectroscopy (HRMS). Both of these techniques may be used extensively for analysis of non-volatile materials not amenable to GC. HRMS may also have application to various volatile materials as well.

### 1. Low Resolution Mass Spectroscopy

A low resolution mass spectrometer is typically capable of resolving differences in mass on the order of 1 part per thousand. This is equivalent to measuring individual m/e values to within ±0.1 to 0.5 mass units for the normal range of organic ions. An LRMS instrument is the type usually used as a detector in GC/MS systems.

The use of LRMS data to determine the structure of single compounds is the mode of mass spectrometry which is most familiar in organic chemistry. As discussed in section E (above), electron impact ionization, which leads to extensive fragmentation of parent (or molecular) ions is usually used to generate spectra for comparison with library reference spectra. The library spectra may be in hard copy (e.g., "Eight Peak Index of Mass

Spectra," 1st ed., Imperial Chemical Industries, Ltd., Mass Spectrometery Data Center, Alder Maston, Reading, United Kingdom, 1970) or in computerized data bases (e.g., EPA/NIH MSSS file or STIRS). The use of LRMS data in interpreting spectra of mixtures of compounds as in complex environmental samples, in addition relies on chemical ionization or low voltage electron impact ionization. These techniques minimize fragmentation and facilitate the identification of various sample components by their respective molecular ions. Particular features of the EI mass spectrum, such as the intense double ionization of polynuclear aromatic hydrocarbons, also aid in interpreting LRMS spectra of mixtures.

Samples may be introduced into the LRMS instrument via either the batch inlet or the direct insertion probe. The batch inlet is used for samples with fairly volatile components that would be lost if the solvent were evaporated. The lower limit for reliable detection of individual sample components for batch inlet spectra is on the order of 1 μg. This requires a concentration of about 500 ppm in the concentrated sample extract, since only 1-2 μL of solvent is routinely injected. The direct insertion probe is used for moderately volatile components. The absolute quantity of sample taken is between 1 ng and 1 μg, but there is no intrinsic limit on the volume of solution that can be dried onto the probe. The temperature of the direct insertion probe can be programmed to drive progressively more non-volatile species into the analyzer. At very high probe temperatures, sample decomposition can occur; this is frequently indicated by the reappearance of material with low molecular weights at probe temperatures inconsistent with their volatility.

For complex environmental samples, such as fractions from preliminary LC or HPLC separations, LRMS can indicate molecular weight ranges and probable chemical class assignments (aliphatic, aromatic, alkylphenols, etc...). Individual chemical compound identifications on the basis of LRMS may not be possible, to any high degree of certainty, for many of these complex mixtures.

### 2. High Resolution Mass Spectrometry

A high resolution mass spectrometer is capable of measuring masses of ions in the spectrum with an accuracy of better than 0.001 atomic mass unit. Data from an HRMS analysis are reported to four decimal places in m/e. The high accuracy and precision makes it possible to take advantage of the mass defect characteristic of atoms and use their exact masses to compute elemental composition assignments for the observed ions. The theoretical mass can be calculated for all plausible* combinations of elements corresponding to a given mass. The theoretical and measured masses are then compared and a "match" is identified when they agree to within a specified value, typically 0.002 or 0.003 amu.

In the simple case where HRMS is being used to confirm or deny the presence of a particular sample component, such as benzopyrene, it is sufficient to calculate the exact theoretical mass expected for $C_{20}H_{12}$ and see if there is a measured m/e value in the sample spectrum within 0.002 or 0.003 amu of the calculated value. This type of static peak matching to preset values (equivalent to the selected ion monitoring mode of LRMS) has a realistic detection limit on the order of 1 ng. For dynamic peak matching or scanning of the HRMS, a limit of about 1 μg is more realistic. These detection limits are typical ones for HRMS instruments utilizing electrical detection. With photographic (photoplate) detection of ions, HRMS spectra can be recorded for samples on the order of 1 ng.

There are a number of other ways in which HRMS data may be of value in the Level 2 analysis of complex organic samples. These involve the use of computer software systems to aid in interpretation of the large quantity of data (500-2000 precisely determined masses of ions with estimated abundances) that is accumulated in an HRMS run. One approach to interpreting these data is to sort the assigned elemental compositions into classes according to heteroatom composition and degree of hydrogen unsaturation (rings plus double bonds or R + DB). An alternative approach is to compare the set of measured masses with theoretical masses calculated for a list of reference compounds. The utility of these reference compound file searching procedures is obviously dependent on maintaining a relevant and appropriately comprehensive library of listed compounds and masses. If the list were as extensive as, for example, the MSSS file of LRMS spectra, the potential usefulness of HRMS file-matching in Level 2 organic analysis would be great indeed. This approach has the advantage that data interpretation can be made identical from laboratory to laboratory, and thus results of different EA's can be more readily compared.

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* Limits for determining "plausible" combinations are set by the user in each application.

HRMS methods are expected to be widely used in Level 2 analysis of nonvolatile polar components separated by LC and HPLC methods.

## G. Infrared Spectroscopy (IR)

Infrared spectroscopy was once the most widely used tool for identification of organic compounds. Absorption in the IR range is due to vibrational energy transitions and virtually every organic species (and many inorganic species) has at least one absorption band in the normal IR frequency range (4000 to 400 $cm^{-1}$). The fact that various functional groups absorb characteristic IR frequencies, rather independently of other portions of the molecular structure, is one of the distinctive features of IR spectroscopy.

In conventional, dispersive IR spectroscopy, a monochromator is used to scan vibrational frequencies and generate a plot of absorption (or transmittance) versus frequency. Modern, dispersive IR instruments, suitable for Level 2 organic analysis, utilize grating monochromators to achieve high resolution ($<1.5$ $cm^{-1}$ at 3000 $cm^{-1}$) and high wavelength accuracy (3 $cm^{-1}$ at 3000 $cm^{-1}$). Most are equipped with ordinate expansion capability and some are specifically designed for interfacing with automatic data processing systems for spectral subtraction and other data manipulations. Dispersive IR instruments are by far the most common types available. Sample size requirements for dispersive IR are on the order of 1 mg for a KBr macropellet or salt plate or about 100 μg for a KBr micropellet in an instrument equipped with a beam condenser and/or ordinate expansion capability.

Individual sample components amounting to <5-10% of the total sample are likely to remain undetected.

A considerable improvement in sensitivity is made possible by the use of Fourier transform infrared spectroscopy (FT-IR) in which an interferometer is used to generate the spectral information. The dedicated computer system that is an integral part of an FT-IR instrument facilitates procedures such as subtraction of "background" spectra. Sample sizes in the range of 1 to 10 μg can be used in FT-IR, which has lower detection limits for individual components on the order of 0.1-1 μg (10%). The FT-IR instruments are not yet widely available; an estimated 75 units were in use worldwide in 1976 compared to more than 50,000 dispersive units. Nevertheless, the potential usefulness of FT-IR in Level 2 organic analysis seems clear.

IR spectra, whether conventional or FT-IR, will be a major tool in the characterization of non-volatile organic species in Level 2. In the general case, when the sample is a fairly complex mixture of compounds, The IR spectrum is primarily useful as an indicator of functional groups present in the sample. It will usually not be possible to determine how these functional groups are combined into various compound classes. In those specific instances where one or only a small number of components are present (as, for example, in an HPLC fraction) it may be possible to interpret the IR spectrum in terms of compound structure. If it is possible to identify a one-to-one match between bands in the sample spectrum and those in a reference spectrum of a known material, this is convincing evidence of compound identity. It can be expected that such instances will be extremely rare in Level 2 analyses.

## H. Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy (NMR) as an organic analysis technique has many similarities to IR spectroscopy in the type of information provided and in the potential applicability to Level 2. The NMR spectrum arises when nuclei with magnetic dipoles, or non-zero spin number, undergo radiofrequency transitions in the presence of an external magnetic field. Common nuclei with spin number 1/2 whose NMR spectra are useful in organic analysis are: $^{1}H$, $^{19}F$, $^{13}C$ and $^{31}P$. The utility of NMR in organic analysis is increased because the transition frequency (chemical shift) of a given nucleus depends not only on the magnitude of the applied, external magnetic field, but also on the local magnetic field generated by adjacent nuclei.

Proton NMR has been most widely investigated for organic analysis, since most organic species have an abundande of $^1H$ nuclei. In the NMR spectra of mixtures, inferences about functional groups present in the sample may be drawn from the absence or presence and intensity of peaks in these varying shift ranges. In those special cases where only one or a few components are present in the sample (as in an HPLC fraction), the fine structure (spin-spin coupling) in the proton NMR spectrum can also aid in interpretation. For conventional, continuous wave proton NMR, milligram (5-50) quantities of sample are required. A time averaging computer can be used to reduce the lower detection limit by about a factor of ten, at the expense of a considerable increase in analysis time to 20-30 hours/sample. The use of pulsed Fourier transform (FT) NMR techniques can dramatically improve the sensitivity to a lower detection limit of about 10 μg of sample by decreasing the scan time per spectrum.

Determination of $^{13}C$ NMR spectra in samples with natural abundance of $^{13}C$ (i.e., 1.1% of total carbon) are done almost exclusively in the Fourier transform mode of operation. Because of the low natural abundance, milligram quantities of sample are required for $^{13}C$ FT-IR. The chemical shift range of $^{13}C$ is about thirty times greater than that of $^1H$, so considerably greater resolution is possible in $^{13}C$ NMR spectra.

It is anticipated that NMR spectroscopy will be a valuable tool in characterizing materials that are not sufficiently volatile for GC analysis or mass spectroscopy in Level 2. In many cases, sample size limitations may restrict the use of NMR to proton Fourier transform methods. In other cases, however, there may be sufficient sample to also acquire $^{13}C$ FT-NMR spectra. The combination of $^1H$ and $^{13}C$ spectra combined with IR data will probably provide the best method of characterizing high molecular weight, non-volatile species in Level 2 organic analysis.

## I. Ultraviolet (UV) and Luminescence Spectroscopy (LS)

Both ultraviolet (UV) and luminescence spectroscopy (LS) are primarily quantitative tools to be used for the measurement of the amount of a species present either directly, after separation, or through color development with a suitable reagent. UV is still considered by many to be the only unequivocal method for distinguishing the various polynuclear aromatic hydrocarbon carcinogens, after they have been isolated by LC, HPLC, TLC or GC. The value of this technique is enhanced by the existence of extensive compilations of reference spectra, including those of nearly all the known carcinogenic urban air pollutants.

LS is a qualitative and quantitative tool for determination of compounds which exhibit fluorescence or phosphorescence. It is especially useful for analysis of polynuclear aromatic hydrocarbons which are strongly fluorescent. The method is sensitive to impurities, to light scatter, a and to side reactions such as photodecomposition of the analyte and quenching of luminescence by oxygen. It has, nevertheless, found wide acceptance in PAH analysis.

In Level 2 organic analysis it is probable that GC/MS and/or HPLC methods will be used in most cases as an alternative to quantitative analysis by UV or LS methods.

# APPENDIX A

## Expected Distribution of MEG Category Organic Compounds
## In
## Level 1 Sampling and Systems Procedures

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## Appendix A

### Expected Distribution of MEG Category Organic Compounds In Level 1 Sampling and Systems Procedures

Each compound in the MEG list of organic compounds (8) has been reviewed to estimate where that sample would be collected in the Level Sampling and Analysis procedure. The attached charts reflect those estimates based on the information currently available. The revised Level 1 procedure has been used as the basis for the review. The estimates for many of the compounds are somewhat speculative, having been derived by analogy to known compounds, rather than being based upon actual experimental data.

Some additional data, such as molecular weight (MW), elemental composition (COMP) and boiling point (BP) were included to assist in studies of these compounds. The health effects-related MATE values for air and water were also included where available.

A compound was defined as a gas to be analized with the field GC if the boiling point was less than 100°C. Volatile compounds analyzed by the TCO procedure are those which have boiling points in the range of 100 to 300°C. The non-volatile materials analized by the GRAV procedure are those with boiling points greater than 300°C.

| Category 1 | MATE | | MW² | BP | COMP | Air | | SGC | Field GC<br>GC Range | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Aliphatic Hydrocarbons | | | | | | | | | | | | | | | | | | | | | | | | | |
| A. Alkanes and Cyclic Alkanes | | | | | | | | | | | | | | | | | | | | | | | | | |
| Methane | 3.3E5 | 4.9E7 | 16 | −161 | $CH_4$ | ● | | | ● | | | | | | | | | | | | | | | | |
| Ethane | 6.1E6 | 9.2E7 | 30 | −89 | $C_2H_6$ | ● | | | | ● | | | | | | | | | | | | | | | |
| Propane | 9.0E6 | 1.4E8 | 44 | −42 | $C_3H_8$ | ● | | | | | ● | | | | | | | | | | | | | | |
| Butanes | 1.4E6 | 2.1E7 | 58 | 0 | $C_4H_{10}$ | ● | | | | | | ● | | | | | | | | | | | | | |
| Pentanes | 1.8E6 | 2.7E7 | 72 | 25± | $C_5H_{12}$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Cyclopentanes | | | 70 | 50 | $C_5H_{10}$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Hexanes | 3.6E5 | 5.4E6 | 86 | 60± | $C_6H_{14}$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Cyclohexanes | 1.1E6 | 1.6E7 | 84 | 81 | $C_6H_{12}$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Heptanes | 1.6E6 | 2.4E7 | 100 | 90± | $C_7H_{16}$ | ● | | | | | | | | | ● | | ● | | | | | | | | |
| Octanes | 1.5E6 | 2.2E7 | 114 | 110± | $C_8H_{18}$ | | ● | | | | | | | | ● | | ● | | | | | | | | |
| Nonanes | 1.1E6 | 1.6E7 | 128 | 150± | $C_9H_{20}$ | | ● | | | | | | | | ● | | ● | | | | | | | | |
| Alkanes (C > 9) | | | | 170+ | $C > 9$ | | ● | | | | | | | | ● | | ● | | | | | | | | |
| B. Alkenes, Cyclic Alkenes and Dienes | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ethylene | 5.7E6 | 8.6E7 | 28 | −104 | $C_2H_4$ | ● | | | ● | | | | | | | | | | | | | | | | |
| Propylene | 8.6E6 | 1.3E8 | 42 | −47 | $C_3H_6$ | ● | | | | ● | | | | | | | | | | | | | | | |
| Butylenes | | | 56 | −5± | $C_4H_8$ | ● | | | | | ● | | | | | | | | | | | | | | |
| Butadienes | 2.2E6 | 3.3E7 | 54 | −5 | $C_4H_6$ | ● | | | | | ● | | | | | | | | | | | | | | |
| Pentenes | | | 70 | 37 | $C_5H_{10}$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Cyclopentadienes | 2.0E5 | 3.0E6 | 66 | 40 | $C_5H_6$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Hexenes | | | 84 | 68 | $C_6H_{12}$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Cyclohexene | 1.0E6 | 1.5E7 | 82 | 83 | $C_6H_{10}$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Cyclohexadiene | | | 80 | 80 | $C_6H_8$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Heptenes | | | 98 | 95± | $C_7H_4$ | ● | | | | | | | | ● | ● | | ● | | | | | | | | |
| C. Alkynes | | | | | | | | | | | | | | | | | | | | | | | | | |
| Acetylene | 5.3E6 | 8.0E7 | 26 | −84 | $C_2H_2$ | ● | | | ● | | | | | | | | | | | | | | | | |
| Propyne | 1.7E6 | 2.5E7 | 40 | −23 | $C_3H_4$ | ● | | | | ● | | | | | | | | | | | | | | | |
| Butyne | | | 54 | −8 | $C_4H_6$ | ● | | | | ● | | | | | | | | | | | | | | | |

1 Health effects basis (μg/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

2-27-78

Category 7

Field GC

| Alkyl Halides | MATE | | MW[2] | BP | COMP | Air | | SGC | GC Range | | | | | | TCO[3] | GRAV[4] | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air[1] | Water | | °C | | Gas | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| A. Saturated Alkyl Halides | | | | | | | | | | | | | | | | | | | | | | | | | |
| Methyl bromide | 6.0E4 | 9.0E5 | 94 | 3 | $CH_3Br$ | ● | | | | | | ● | | | | | | | | | | | | | |
| Methyl chloride | 2.1E5 | 3.2E6 | 50 | −24 | $CH_3Cl$ | ● | | | | | ● | | | | | | | | | | | | | | |
| Methyl iodide | 8.5E2 | 1.3E4 | 142 | 42 | $CH_3I$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Dichloromethane (methylene | 2.6E5 | 3.9E6 | 84 | 40 | $CH_2Cl_2$ | ● | | | | | | | ● | | | | | | | | | | | | |
| chloride) | | | | | | ● | | | | | | | | | | | | | | | | | | | |
| Bromodichloromethane | | | 162 | 89 | $CHCl_2Br$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Dibromochloromethane | | | 206 | 118 | $CHClBr_2$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Tribromomethane (bromoform) | 5.0E3 | 7.5E4 | 250 | 150 | $CHBr_3$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Dibromodichloromethane | | | 240 | 135 | $CCl_2Br_2$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Dichlorodifluoromethane | 5.0E6 | 7.4E7 | 120 | −30 | $CCl_2F_2$ | ● | | | | | ● | | | | | | | | | | | | | | |
| Trichlorofluoromethane | 5.6E6 | 8.4E7 | 136 | 25 | $CCl_3F$ | ● | | | | | | ● | | | | | | | | | | | | | |
| Carbon tetrachloride | 6.0E4 | 9.0E5 | 152 | 77 | $CCl_4$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 1,2-dichloroethane (ethylene chloride) | 2.0E5 | 3.0E6 | 98 | 84 | $C_2H_4Cl_2$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 1,1,1,-trichloroethane (methyl chloroform) | 4.5E4 | 6.8E5 | 132 | 74 | $C_2H_3Cl_3$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 1,2-dichloro-1,2-difluoro ethane | 5.0E6 | 7.4E7 | 134 | – | $C_2H_2Cl_2F_2$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Hexachloroethane | 1.0E4 | 1.5E5 | 234 | 186 | $C_2Cl_6$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Dichloropropanes | 3.5E5 | 5.3E6 | 112 | 90± | $C_3H_6Cl_2$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Bromobutanes | | | 136 | 100± | $C_4H_9Br$ | ● | | | | | | | | ● | ● | | | ● | | | | | | | |
| Hexachlorocyclohexane (lindane) | 5.0E2 | 7.5E3 | 288 | – | $C_6Cl_6$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| 1-chlorooctane | | | 148 | 182 | $C_8H_{17}Cl$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| B. Unsaturated Alkyl Halides | | | | | | | | | | | | | | | | | | | | | | | | | |
| Chloroethene (vinyl chloride) | 2.6E3 | 3.8E4 | 62 | −13 | $C_2H_3Cl$ | ● | | | | | ● | | | | | | | | | | | | | | |
| 1,2-dichloroethene | 7.0E5 | 1.1E7 | 96 | 60 | $C_2H_2Cl_2$ | ● | | | | | | | ● | | | | | | | | | | | | |
| 1,1-dichloroethene | 2.6E5 | 3.9E6 | 96 | 37 | $C_2H_2Cl_2$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Tetrachloroethene (per-(chloroethylene) | 6.7E5 | 1.0E7 | 164 | 121 | $C_2Cl_4$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Dichloropropenes | 1.1E4 | 1.7E5 | 110 | 80± | $C_3H_4Cl_2$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Hexachlorobutadiene | 4.1E3 | 6.1E4 | 258 | 215 | $C_4Cl_6$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Hexachlorocyclopentadiene | 1.1E2 | 1.7E3 | 270 | 240 | $C_5Cl_6$ | | ● | | | | | | | | ● | | | ● | | | | | | | |

1 Health effects basis (μg/m³) 2 Monoisotopic: lightest isotope of each atom 3 TCO BP 100–300°C 4 GRAV BP >300°C

2-27 IE

Category 3

Ethers

Field GC

| | MATE | | MW² | BP | COMP | Air | | SGC | GC Range | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| 2,2'-Oxy bis propane | 1.1E6 | 1.6E7 | 102 | 90 | $C_6H_{14}O$ | ● | | | | | | – | ● | – | | | | | | | | | | | |
| 2-Ethyl-4-methyl-1,3- | 2.3E4 | 3.4E5 | 116 | 118 | $C_6H_{12}O$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| Dioxolanes | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,3-Dioxane | 1.8E5 | 2.7E6 | 88 | 105 | $C_4H_8O$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| 1,4-Dioxane | 1.8E5 | 2.7E6 | 88 | 101 | $C_4H_8O$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| 2-Methoxy biphenyl | | | 184 | 274 | $C_{13}H_{12}O$ | | ● | | | | | | | | ● | | | | | ● | | | | | |

1 Health effects basis (µg/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100 300°C 4 GRAV BP > 300°C

2-27-78

Category 4

| | MATE | | MW² | BP | COMP | Air | | Field GC | | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | SGC | GC Range | | | | | | | | | | | | | | | | |
| Halogenated Ethers | Air¹ | Water | | °C | | Grab | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Chloromethyl methyl ether | 3.7E4 | 5.5E5 | 80 | 56 | $C_2H_5OCl$ | ● | | | | | | | ● | | | | | | | | | | | | |
| 1,1'-Dichloromethyl ether | | | 114 | 105 | $C_2H_4OCl_2$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| 2-Chloro-1,3-epoxypropane | | | 92 | SOLID | $C_3H_5OCl$ | | ● | | | | | | | | | ● | | | | ● | | | | | |
| 2-Chloroethylmethyl ether | | | 94 | 92 | $C_3H_7OCl$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 1-Chloro-1,3-oxetane | | | 92 | — | $C_3H_5OCl$ | | ● | | | | | | | | | ● | | | | ● | | | | | |
| Chloromethylethyl ether | | | 94 | 80 | $C_3H_7OCl$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Chloro ethyl ethyl ether | | | 108 | 100± | $C_4H_9OCl$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| 1,1'-Dichlorodiethyl ether | 3.0E4 | 4.5E5 | 142 | 116 | $C_4H_8OCl_2$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| 1,2-Dichlorodiethyl ether | | | 142 | 140 | $C_4H_8OCl_2$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| 1,2-Dichloroethyl ethyl ether | | | 142 | 145 | $C_4H_8OCl_2$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| 2,2'-Dichlorodiethyl ether | 3.0E4 | 4.5E5 | 142 | 178 | $C_4H_8OCl_2$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| α-Chlorobutylethyl ether | | | 136 | — | $C_6H_{13}OCl$ | | ● | | | | | | | | | ● | | | | ● | | | | | |
| bis-(1-chloroisopropyl)ether | | | 170 | — | $C_6H_{12}OCl_2$ | | ● | | | | | | | | | ● | | | | ● | | | | | |
| 1,2-Dichlorodiisobutyl ether | | | 190 | — | $C_8H_{16}OCl_2$ | | ● | | | | | | | | | ● | | | | ● | | | | | |
| Bromophenyl phenyl ether | | | 248 | 310 | $C_{12}H_9OBr$ | | ● | | | | | | | | | ● | | | | ● | | | | | |

1 Health effects basis (µg/m³) ; Monoisotopic, lightest isotope of each atom  3 TCO BP 100 300°C  4 GRAV BP 300°C

2-27-78

Category 5

| Alcohols | MATE Air[1] | MATE Water | MW[2] | BP °C | COMP | Air Gas | Air SASS | Field GC SGC | GC Range 1 | 2 | 3 | 4 | 5 | 6 | TCO[3] | GRAV[4] | LC Fraction 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A. Primary Alcohols | | | | | | | | | | | | | | | | | | | | | | | | | |
| Methyl alcohol | 2.6E5 | 3.9E6 | 32 | 64 | $CH_3OH$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Ethyl alcohol | 1.9E6 | 2.9E7 | 46 | 78 | $C_2H_5OH$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 1-propanol | 5.0E5 | 7.5E6 | 60 | 97 | $C_3H_7OH$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 1-butanol | 1.5E5 | 2.3E6 | 74 | 118 | $C_4H_9OH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 1-pentanol | 3.6E5 | 5.4E6 | 88 | 138 | $C_5H_{11}OH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| B. Secondary Alcohols | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2-propanol | 9.8E5 | 1.5E7 | 60 | 82 | $C_3H_7OH$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 2-butanol | 4.5E5 | 6.8E6 | 74 | 99 | $C_4H_9OH$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 2-pentanol; 3-pentanol | 3.6E5 | 5.4E6 | 88 | 120 | $C_5H_{11}OH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| α-hydroxytoluene | 5.5E4 | 8.3E5 | 108 | 205 | $C_7H_7OH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 2,6-dimethyl-4-heptanol | 1.6E5 | 2.4E6 | 144 | 178 | $C_9H_{19}OH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Borneol | 9.0E4 | 1.4E6 | 154 | 212 | $C_{10}H_{17}OH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| C. Tertiary Alcohols | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2-methyl propanol (tert-butyl alcohol) | 3.0E5 | 4.5E6 | 74 | 82 | $C_4H_9OH$ | ● | | | | | | | | ● | | | | | | | | | | | |
| α-methyl-αhydroxytoluene | 1.8E4 | 2.7E5 | 122 | — | $C_8H_9OH$ | | ● | | | | | | | | | ● | | | | | | ● | | | |
| α-terpineol | 1.9E5 | 2.9E6 | 154 | 220 | $C_{10}H_{17}OH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Isoborneol | | | 154 | SOLID | $C_{10}H_{17}OH$ | | ● | | | | | | | | | ● | | | | | | ● | | | |

1 Health effects basis (μg/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

2-23-78

Category 6

|  | MATE |  | MW² | BP | COMP | Air |  | Field GC |  |  |  |  |  |  | TCO³ | GRAV⁴ | LC Fraction |  |  |  |  |  |  |  | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | SGC | GC Range |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | Air¹ | Water |  | °C |  | Gas | SASS |  | 1 | 2 | 3 | 4 | 5 | 6 |  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |  |
| Glycols, Epoxides |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| A. Glycols |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Ethylene glycol (1,2-Ethanediol)) | 1.0E4 | 1.5E5 | 62 | 198 | $C_2H_6O_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Propylene glycol (1,2-Propanediol)) | 3.6E5 | 5.4E6 | 76 | 188 | $C_3H_8O_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| B. Epoxides |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 2,3-epoxy-1 propanol | 1.5E5 | 2.3E6 | 74 | 166 | $C_3H_6O_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| 1-chloro-2,3-epoxy propane (α-Epichlorohydrin) | 1.6E4 | 2.4E5 | 92 | 116 | $C_3H_5ClO$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |

1 Health effects basis (µg/m³) 2 Monoisotopic, lightest isotope of each atom    3 TCO BP 100 - 300°C    4 GRAV BP > 300°C

2-27-78

Category 7

## Aldehydes, Ketones

| | MATE | | MW² | BP | COMP | Air | | Field GC | | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | SGC | GC Range | | | | | | | | | | | | | | | | |
| | | | | | | | | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| **A. Aldehydes*** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Formaldehyde | 1.6E3 | 2.4E4 | 30 | −21 | $CH_2O$ | ● | | | | | ● | | | | | | | | | | | | | | |
| Acetaldehyde | 1.8E5 | 2.7E6 | 44 | 20 | $C_2H_4O$ | ● | | | | | | ● | | | | | | | | | | | | | |
| Propionaldehyde | 3.6E4 | 5.4E5 | 58 | 50 | $C_3H_6O$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Acrolein | 2.5E2 | 3.8E3 | 56 | 52 | $C_3H_4O$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Butyraldehyde | 1.1E5 | 1.7E6 | 72 | 75 | $C_4H_8O$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Bromoform butanal | | | 306 | — | $C_4H_6OBr_3$ | | ● | | | | | | | | | ● | | | | ● | | | | | |
| 3-Methylbutanal | 3.9E5 | 5.8E6 | 86 | 92 | $C_5H_{10}O$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Benzaldehyde | 5.9E4 | 8.8E5 | 106 | 179 | $C_7H_6O$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| **B. Ketones** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Acetone | 2.4E6 | 3.6E7 | 58 | 56 | $C_3H_6O$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Tetrachloroacetone | | | 194 | 180 | $C_3H_2OCl_4$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| Butanone | 5.9E5 | 8.9E6 | 72 | 80 | $C_4H_8O$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Isophrone | 2.5E4 | 3.8E5 | 138 | 215 | $C_9H_{14}O$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| Camphor (d) | 1.2E4 | 1.8E5 | 152 | 204 | $C_{10}H_{16}O$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| Acetophenone | 4.1E4 | 6.1E5 | 120 | 202 | $C_8H_8O$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| Chlorohydroxy benzophenone | | | 233 | — | $C_{13}H_9O_2Cl$ | | ● | | | | | | | | | ● | | | | ● | | | | | |
| 5,6-Benzo-9-anthrone | | | 244 | — | $C_{18}H_{12}O$ | | ● | | | | | | | | | ● | | | | ● | | | | | |
| Dihydro(d)carbone | | | 152 | 221 | $C_{10}H_{16}O$ | | ● | | | | | | | | ● | | | | | ● | | | | | |

1 Health effects basis (ug/m³) 2 Mono-isotopic lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

2-27-78

Category 8

| Carboxylic Acids and Derivatives | MATE Air¹ | MATE Water | MW² | BP °C | COMP | Air Gas | Air SASS | Field GC SGC | GC Range 1 | 2 | 3 | 4 | 5 | 6 | TCO³ | GRAV⁴ | LC Fraction 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A. Carboxylic Acids | | | | | | | | | | | | | | | | | | | | | | | | | |
| Formic acid | 9.0E3 | 1.4E5 | 46 | 100 | $CH_2O_2$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| Acetic acid | 2.5E4 | 3.0E5 | 60 | 117 | $C_2H_4O_2$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| Maleic acid | 1.0E3 | 1.5E4 | 116 | 138 | $C_4H_4O_4$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| Benzoic acid | 1.4E5 | 2.1E6 | 122 | 249 | $C_7H_6O_2$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| Phthalic acid | 6.0E3 | 9.0E4 | 166 | solid | $C_8H_6O_4$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| Long chain acids | | | | 300-380 | $C_{12}-C_{18}$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| B. Carboxylic Acids with Additional Functional Groups | | | | | | | | | | | | | | | | | | | | | | | | | |
| Hydroxyacetic acid | 8.8E4 | 1.3E6 | 76 | solid | $C_2H_4O_3$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| Hydroxybenzoic acids | 4.0E4 | 6.0E5 | 138 | solid | $C_7H_6O_3$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| 3-hydroxypropanoic acid lactone | 3.2E2 | 4.8E3 | 72 | 162 | $C_3H_4O_2$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| C. Amides | | | | | | | | | | | | | | | | | | | | | | | | | |
| Formamide | 3.0E4 | 4.5E5 | 45 | 210 | $CH_3NO$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| Acetamide | 4.5E5 | 6.8E6 | 59 | 221 | $C_2H_5NO$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| 6-aminohexanoic acid | | | 131 | solid | $C_6H_{13}NO_2$ | | ● | | | | | | | | | ● | | | | | | | | ● | |
| D. Esters | | | | | | | | | | | | | | | | | | | | | | | | | |
| Methyl methacrylate | 4.1E5 | 6.2E6 | 100 | 100 | $C_5H_8O_2$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Phthalates | 5.0E3 | 7.5E4 | | 280° | | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Adipates | 1.9E4 | 2.8E5 | | 110-175 | | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Long chain esters | | | | — | | | | | | | | | | | | | | | | | | | | | |
| Methyl benzoate | 1.5E5 | 2.6E6 | 136 | 200 | $C_8H_8O_2$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Phenyl benzoate | | | 198 | 314 | $C_{13}H_{10}O_2$ | | ● | | | | | | | | | ● | | | | | | ● | | | |
| Di-2-ethylhexyl phthalate | | | 279 | 231 | $C_{24}H_{38}O_4$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 6-Aminohexanoic acid (e-caprolactam) | 1.0E3 | 1.5E4 | 112 | solid | $C_6H_{11}NO$ | | ● | | | | | | | | | ● | | | | | | | ● | | |

2-27-78

1 Health effects basis (µg/m³) 2 Mono-isotopic, lightest isotope of each atom  3 TCO BP 100-300°C  4 GRAV BP >300°C

Category 9

**Nitriles**

|  | MATE |  | MW[2] | BP | COMP | Air |  | Field GC |  |  |  |  |  |  | TCO[3] | GRAV[4] | LC Fraction |  |  |  |  |  |  |  | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Air[1] | Water |  | °C |  | Gas | SASS | SGC | GC Range 1 | 2 | 3 | 4 | 5 | 6 |  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |  |
| Acetonitrile | 7.0 E4 | 1.1 E6 | 41 | 81 | $C_2H_3N$ | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |
| 1-Cyanoethane (acrylonitrile) | 4.5E4 | 6.8E5 | 53 | 77 | $C_3H_3N$ | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |
| 1,4-Dicyano-1-hydroxy butane |  |  | 124 | >500 | $C_6H_8ON_2$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Benzonitrile | 3.2E4 | 9.9E5 | 103 | 191 | $C_7H_5N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |  |
| Naphthonitriles |  |  | 153 | 300± | $C_{11}H_7N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  | ● |  |  |  |  |  |

[1] Health effects basis (µg/m³) [illegible] lightest isotope of each atom

[3] TCO BP 100-300°C

[4] GRAV BP >300°C

2 27 78

Category 10

Amines

Field GC

| | MATE | | MW² | BP | COMP | Air | | SGC | GC Range | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| **A. Primary Amines** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ethylamine | 1.0E4 | 2.7E5 | 45 | 16 | $C_2H_7N$ | ● | | | | | | ● | | | | | | | | | | | | | |
| Ethanolamine | 6.0E3 | 9.0E4 | 61 | 171 | $C_2H_7NO$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 3-Aminopropene | | | 57 | 58 | $C_3H_7N$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Propanolamine | 1.3E5 | 1.9E6 | 75 | 160 | $C_3H_9NO$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 1-Aminobutane | 1.5E4 | 2.3E5 | 75 | 78 | $C_4H_{11}N$ | ● | | | | | | | | ● | | | | | | | | | | | |
| 2-Aminobutane | 1.5E4 | 2.3E5 | 75 | 63 | $C_4H_{11}N$ | ● | | | | | | | | ● | | | | | | | | | | | |
| Cyclohexylamine | 4.0E4 | 6.0E5 | 99 | 134 | $C_6H_{13}N$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 1,2-Diaminoethane | 2.5E4 | 3.8E5 | 60 | 116 | $C_2H_8N_2$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Aniline | 1.9E4 | 3.0E5 | 93 | 184 | $C_6H_7N$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 2-Aminotoluene | 1.1E2 | 1.7E3 | 107 | 200 | $C_7H_9N$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Dimethylaniline | 2.5E4 | 3.8E5 | 121 | 193 | $C_8H_{11}N$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Anisidines | 5.0E2 | 7.5E3 | 123 | 240± | $C_7H_9NO$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Aminodiphenyls | 1.3E3 | 2.0E4 | 169 | 300± | $C_{12}H_{11}N$ | | ● | | | | | | | | | ● | | | | | | ● | | | |
| Aminonaphthalenes | 5.6E2 | 8.5E3 | 143 | 300+ | $C_{10}H_9N$ | | ● | | | | | | | | | ● | | | | | | ● | | | |
| 1,4-Diaminobenzene | 4.5E3 | 6.8E4 | 104 | 267 | $C_6H_8N_2$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 4,4'-Diaminodiphenyl | 1.4E4 | 2.1E5 | 184 | 400 | $C_{12}H_{12}N_2$ | | ● | | | | | | | | | ● | | | | | | ● | | | |
| 3,3'-Dichlorobenzidine | 6.6E3 | 9.9E4 | 224 | [illegible] | $C_{12}H_{10}Cl_2$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| 4,4'-Methylene bis (2-chloroaniline) | 2.2E2 | 3.3E3 | 266 | [illegible] | $C_{13}H_{12}N_2Cl_2$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| **B. Secondary Amines** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ethyleneimine | 3.3E2 | 5.0E3 | 43 | 57 | $C_2H_5N$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Dimethylamine | 1.8E4 | 2.7E5 | 45 | 7 | $C_2H_7N$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Ethylmethylamine | | | 59 | / | $C_3H_9N$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Diethylamine | 7.5E4 | 1.1E6 | 73 | 56 | $C_4H_{11}N$ | ● | | | | | | | ● | | | | | | | | | | | | |
| Morpholine | 7.0E4 | 1.1E6 | 87 | 129 | $C_4H_9N$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| **C. Tertiary Amines** | | | | | | | | | | | | | | | | | | | | | | | | | |
| N,N-Dimethylaniline | 2.5E4 | 3.8E5 | 121 | 194 | $C_8H_{11}N$ | | ● | | | | | | | | ● | | | | | | | ● | | | |

2-27-78

1 [illegible] (µg/m³) 2 [illegible] lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

Category 11

**Azo Compounds, Hydrazine,**

**and Derivatives**

|  | MATE |  | MW[2] | BP | COMP | Air |  | Field GC |  |  |  |  |  |  | TCO[3] | GRAV[4] | LC Fraction |  |  |  |  |  |  |  | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | SGC | GC Range |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | Air[1] | Water |  | °C |  | Gas | SASS |  | 1 | 2 | 3 | 4 | 5 | 6 |  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |  |
| Diazomethane | 4.0E2 | 6.0E3 | 42 | −23 | $CH_2N_2$ | ● |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Hydrazine |  |  |  | 113 | $N_2H_4$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  | ● |  |  |
| Dimethylhydrazines | 1.0E3 | 1.5E4 | 60 | 60-80 | $C_2H_8N_2$ | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |
| Diphenylhydrazines | 1.4E4 | 2.0E5 | 184 | 220 | $C_{12}H_{12}N_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  | ● |  |  |

1 [illegible] (µg/m³) 2 [illegible] of each [illegible]  3 TCO BP 100-300°C  4 GRAV BP >300°C

2-23 78

Category 12

**Nitrosamines**

| | MATE | | MW² | BP | COMP | Air | | SGC | GC Range | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Dimethylamine-N-Nitroso | 1.2E0 | 1.8E1 | 74 | 154 | $C_2H_6N_2O$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| Diethylamine-N-Nitroso | 1.2E2 | 1.8E3 | 102 | 177 | $C_4H_{10}N_2O$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| Dipropylamine-N-Nitroso | 2.4E3 | 3.6E4 | 130 | 206 | $C_6H_{14}N_2O$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| Diisopropylamine-N-Nitroso | 3.8E4 | 5.8E5 | 130 | 194 | $C_6H_{14}N_2O$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| Dipentylamine-N-Nitroso | | | 186 | | $C_{10}H_{22}N_2O$ | | ● | | | | | | | | | ● | | | | | ● | | | | |
| Aniline, N-Methyl-N-Nitroso | 1.3E3 | 1.9E4 | 166 | 225 | $C_7H_8N_2O$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| Diphenylamine-N -Nitroso | 7.4E4 | 1.1E6 | 198 | SOLID | $C_{12}H_{10}N_2O$ | | ● | | | | | | | | | ● | | | | | ● | | | | |

1 [illegible] $(\mu g/m^3)$ [illegible]  3 TCO BP [illegible]  4 GRAV BP [illegible]

2 [illegible]

13

## Mercaptans, Sulfides and Disulfides

| | MATE | | MW² | BP | COMP | Air | | SGC | GC Range | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| **A. Mercaptans** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Methyl mercaptan | 1.0E3 | 1.5E4 | 48 | 6 | $CH_3SH$ | ● | | ● | | | | | | | | | | | | | | | | | |
| Ethyl mercaptan | 1.0E3 | 1.5E4 | 62 | 35 | $C_2H_5SH$ | ● | | ● | | | | | | | | | | | | | | | | | |
| Propyl mercaptans | 8.1E4 | 1.2E6 | 76 | 60± | $C_3H_7SH$ | ● | | ● | | | | | | | | | | | | | | | | | |
| Butyl mercaptans | 1.5E3 | 2.3E4 | 90 | 80± | $C_4H_9SH$ | ● | | ● | | | | | | | | | | | | | | | | | |
| Benzenethiol | 2.1E3 | 3.1E4 | 110 | 168 | $C_6H_5SH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 1-anthrathiol | | | 210 | — | $C_{14}H_9SH$ | | ● | | | | | | | | | ● | | | | | | ● | | | |
| Perchloromethyl mercaptan | 8.0E2 | 1.2E4 | 150 | 149 | $CCl_3SH$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| **B. Sulfides, Disulfides** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Dimethyl sulfide | 2.4E4 | 3.6E5 | 62 | 37 | $C_2H_6S$ | ● | | ● | | | | | | | | | | | | | | | | | |
| Diethyl sulfide | | | 90 | 92 | $C_4H_{10}S$ | ● | | ● | | | | | | | | | | | | | | | | | |
| Phenyl sulfide | 9.6E4 | 1.4E6 | 186 | 296 | $C_{12}H_{10}S$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Methyl disulfide | | | 94 | 116 | $C_2H_6S_2$ | | ● | | | | | | | | ● | | | | | | | ● | | | |

Field GC

1 [illegible] ($\mu g/m^3$) 2 [illegible]

3 TCO BP 100–300°C

4 GRAV BP >300°C

2-27-78

Category 14

| Sulfonic Acids, Sulfoxides | MATE | | MW² | BP | COMP | Air | | Field GC | | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | SGC | GC Ramp 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| **A. Sulfonic Acids** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Benzenesulfonic acid | 4.0E4 | 6.0E5 | 158 | solid | $C_6H_6SO_3$ | | ● | | | | | | | | | ● | | | | | | | | ● | |
| 9,10-Anthraquinone-disulfonic acids | | | 368 | solid | $C_{14}H_6O_2-(SO_3H)_2$ | | ● | | | | | | | | | ● | | | | | | | | ● | |
| **B. Sulfoxides** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Dimethyl sulfoxide | 8.1E2 | 1.2E3 | 78 | 189 | $C_2H_6SO$ | | ● | | | | | | | | ● | | | | | | | | | ● | |

1 Health effects basis ($\mu g/m^3$) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

2-27-78

Category 15

**Benzene, Substituted Benzene**

Hydrocarbons

|  | MATE |  | MW² | BP | COMP | Air |  | Field GC |  |  |  |  |  |  | TCO³ | GRAV⁴ | LC Fraction |  |  |  |  |  |  |  | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | SGC | GC Range |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | Air¹ | Water |  | °C |  | Gas | SASS |  | 1 | 2 | 3 | 4 | 5 | 6 |  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |  |
| Benzene | 3.0E3 | 4.5E4 | 78 | 80 | $C_6H_6$ | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |
| Toluene | 3.8E5 | 5.6E6 | 92 | 110 | $C_7H_8$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Ethyl benzene | 4.4E5 | 6.5E6 | 106 | 136 | $C_8H_{10}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Styrene | 4.2E5 | 6.3E6 | 104 | 145 | $C_8H_8$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Propyl benzene | 2.2E5 | 3.3E6 | 120 | 159 | $C_9H_{12}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Isopropyl benzene | 6.3E4 | 9.5E5 | 120 | 152 | $C_9H_{12}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Butyl benzene | 2.3E5 | 3.4E6 | 134 | 183 | $C_{10}H_{14}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Biphenyls | 1.0E3 | 1.5E4 | 154 | 255 | $C_{12}H_{10}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| 4,4'-diphenylbiphenyl |  |  | 306 | 428 | $C_{24}H_{18}$ |  | ● |  |  |  |  |  |  |  |  | ● |  | ● |  |  |  |  |  |  |  |
| Xylenes | 4.4E5 | 6.5E6 | 106 | 140± | $C_8H_{10}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Dialkyl benzenes | 2.3E5 | 3.4E6 |  | / |  |  | ● |  |  |  |  |  |  |  |  | ● |  | ● |  |  |  |  |  |  |  |
| Tetrahydronaphthalene | 1.3E5 | 2.0E6 | 132 | 207 | $C_{10}H_{12}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Dihydronaphthalene | 1.3E5 | 2.0E6 | 130 | / | $C_{10}H_{10}$ |  | ● |  |  |  |  |  |  |  |  | ● |  | ● |  |  |  |  |  |  |  |
| Terphenyls | 9.0E3 | 1.4E5 | 230 | 350± | $C_{18}H_{14}$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |
| Trimethyl benzenes | 1.2E5 | 1.8E6 | 120 | 170± | $C_9H_{12}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |
| Tetramethyl benzenes |  |  | 134 | 200± | $C_{10}H_{14}$ |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |  |  |  |  |  |  |  |

2-27-78

1 Health effects basis (µg/m³) 2 Monoisotopic: lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

Category 16

| | MATE | | MW[2] | BP | COMP | Air | | Field GC | | | | | | | TCO[3] | GRAV[4] | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air[1] | Water | | °C | | Gas | SASS | SGC | GC Range 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| **Halogenated Aromatic Compounds** | | | | | | | | | | | | | | | | | | | | | | | | | |
| A. Ring Substituted Aromatics | | | | | | | | | | | | | | | | | | | | | | | | | |
| Chlorobenzene | 3.5E5 | 5.3E6 | 112 | 131 | $C_6H_5Cl$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Bromo and dibromobenzenes | | | 156/234 | 150/220 | $C_6H_5Br(2)$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Bromochlorobenzenes | | | 190 | 200± | $C_6H_4BrCl$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| 1,2-dichlorobenzene | 3.0E5 | 4.5E6 | 146 | 179 | $C_6H_4Cl_2$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| 1,3-dichlorobenzene | | | 146 | 172 | $C_6H_4Cl_2$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| 1,4-dichlorobenzene | 4.5E5 | 6.8E6 | 146 | 174 | $C_6H_4Cl_2$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Polychlorinated benzenes | 3.4E4 | 5.1E5 | 282 | HIGH | $C_6Cl_6$ | | ● | | | | | | | | ● | | | | ● | | | | | | |
| Chloronaphthalenes | 6.9E4 | 1.0E6 | 162 | 250+ | $C_{10}H_7Cl$ | | ● | | | | | | | | ● | | | | ● | | | | | | |
| Polychlorinated biphenyls | 5.0E2 | 7.5E3 | | 270+ | | | ● | | | | | | | | ● | | | | ● | | | | | | |
| B. Aromatics with Halogenated Alkyl Side Chain | | | | | | | | | | | | | | | | | | | | | | | | | |
| α-chlorotoluene | 5.0E3 | 7.5E4 | 126 | 180 | $C_7H_7Cl$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| bis-(chloromethyl)-benzene | | | 174 | 240± | $C_8H_8Cl_2$ | | ● | | | | | | | | ● | | | ● | | | | | | | |

2-27 78

1 Health effects basis (ug/m³) 2 Monoisotopic lightest isotope of each atom 3 TCO BP 100 300°C 4 GRAV BP >300°C

Category 17

**Aromatic Nitro Compounds**

| | MATE | | MW² | BP | COMP | Air | | Field GC | GC Range | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | SGC | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Nitrobenzene | 5.0E3 | 7.5E4 | 123 | 210 | $C_6H_5NO_2$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| 4-nitrobiphenyl; nitrobiphenyls | 1.3E3 | 2.0E4 | 199;199 | 200 – | $C_{12}H_9NO_2$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| | | | | 340 | | | ● | | | | | | | | ● | ● | | | | ● | | | | | |
| Chloronitrobenzenes | 1.6E4 | 2.5E4 | 157 | 240± | $C_6H_4ClNO_2$ | | ● | | | | | | | | ● | | | | | ● | | | | | |
| Methoxynitrobenzenes | 4.5E3 | 6.8E4 | 153 | 260± | $C_7H_7NO_3$ | | ● | | | | | | | | ● | | | | | | ● | | | | |
| Dinitrotoluenes | 1.5E3 | 2.3E4 | 182 | 300± | $C_7H_6(NO_2)_2$ | | ● | | | | | | | | | ● | | | | | ● | | | | |

1 Health effects basis (μg/m³) 2 Monoisotopic: lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

Category 18

|  |  |  |  |  |  |  |  | Field GC |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | MATE |  | MW² | BP | COMP | Air |  | SGC | GC Range |  |  |  |  |  | TCO³ | GRAV⁴ | LC Fraction |  |  |  |  |  |  |  | Comments |
| Phenols | Air¹ | Water |  | °C |  | Gas | SASS |  | 1 | 2 | 3 | 4 | 5 | 6 |  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |  |
| A. Monohydrics |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Phenol | 1.9E4 | 5.0E0 | 94 | 182 | $C_6H_6O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Methyl phenols (cresols) | 2.2E4 | 5.0E0 | 108 | 200± | $C_7H_8O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| 2-methoxyl phenol | 3.3E4 | 5.0E0 | 124 | 205 | $C_7H_8O_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Ethylphenols |  |  | 122 | 210± | $C_8H_{10}O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Hydroxybiphenyls | 2.3E4 | 5.0E0 | 170 | 280° | $C_{12}H_{10}O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| 2,2'-dihydroxydiphenyls | 6.8E3 | 5.0E0 | 186 | SOLID | $C_{12}H_{10}O_2$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Dimethylphenols (Xylenols) | 1.3E4 | 5.0E0 | 122 | 220± | $C_8H_{10}O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Polyalkylphenols | 1.5E4 | 5.0E0 |  | HIGH |  |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| B. Dihydrics, Polyhydrics |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 1,2-dihydroxybenzene | 2.0E4 | 5.0E0 | 110 | 245 | $C_6H_6O_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| 1,3-dihydroxybenzene | 4.5E4 | 5.0E0 | 110 | 178 | $C_6H_6O_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| 1,4-dihydroxybenzene | 2.0E3 | 5.0E0 | 110 | 285 | $C_6H_6O_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| 1,2,3-trihydroxybenzenes | 3.6E4 | 5.0E0 | 126 | 309 | $C_6H_6O_3$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| C. Fused ring hydroxy compounds |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| α-naphthanol | 1.2E5 | 5.0E0 | 144 | 278 | $C_{10}H_8O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| β-naphthanol | 1.1E5 | 5.0E0 | 144 | 285 | $C_{10}H_8O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Phenthrols |  | 5.0E0 |  | SOLID |  |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Indanols | 1.5E5 | 5.0E0 | 134 | 255 | $C_9H_{10}O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Acenaphthenols |  | 5.0E0 | 170 | SOLID | $C_{12}H_{10}O$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| 2-hydroxyfluorene |  | 5.0E0 | 182 | SOLID | $C_{13}H_{10}O$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| 2-hydroxydibenzofuran |  | 5.0E0 | 184 | SOLID | $C_{12}H_8O$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |

1 Health effects basis (µg/m³) 2 Mono-isotopic, lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

2-27-78

Category 19

**Halophenols**

| | MATE | | MW² | BP | COMP | Air | | SGC | Field GC | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | | GC Range 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | R | |
| 2-chlorophenol | 3.0E4 | 5.0E0 | 128 | 175 | $C_6H_5OCl$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| 2,4-dichlorophenol | 7.0E3 | 5.0E0 | 162 | 210 | $C_6H_4OCl_2$ | | ● | | | | | | | | ● | | | | | | | ● | | | |
| Pentachlorophenol | 5.0E2 | 5.0E0 | 264 | 310 | $C_6HOCl_5$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| Chlorinated cresols | 2.3E4 | 5.0E0 | 123 | 190⁺ | $C_7H_7OCl$ | | ● | | | | | | | | ● | | | | | | | ● | | | |

1 Health effects based (µg/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100 - 300°C 4 GRAV BP > 300°C

2-27-78

Category 20

**Nitrophenols**

| | MATE | | MW[2] | BP | COMP | Air | | Field GC | | | | | | | TCO[3] | GRAV[4] | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air[1] | Water | | °C | | Gas | SASS | SGC | GC Range 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| 2-nitrophenol | 5.8E4 | 5.0E0 | 139 | 216 | $C_6H_5NO_3$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| 3-nitrophenol | 2.0E4 | 5.0E0 | 139 | 194 | $C_6H_5NO_3$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| 4-nitrophenol | 1.6E4 | 5.0E0 | 139 | 279 | $C_6H_5NO_3$ | | ● | | | | | | | | ● | | | | | | | | ● | | |
| Dinitrophenols | 1.4E3 | 5.0E0 | 184 | solid | $C_6H_4N_2O_5$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| o-cresol, dinitro | 2.0E2 | 5.0E0 | 198 | solid | $C_7H_6N_2O_5$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| p-cresol, dinitro | 6.8E2 | 5.0E0 | 198 | solid | $C_7H_6N_2O_5$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| 2-amino-4,6-dinitrophenol | 4.6E4 | 5.0E0 | 198 | solid | $C_6H_5N_3O_5$ | | ● | | | | | | | | | ● | | | | | | | ● | | |
| Trinitrophenol | 1.0E2 | 5.0E0 | 229 | solid | $C_6H_3N_3O_7$ | | ● | | | | | | | | | ● | | | | | | | ● | | |

1 Health effects basis ($\mu g/m^3$) 2 Mono-isotopic: lightest isotope of each atom 3 TCO BP 100 300°C 4 GRAV BP 300°C

2-27-78

Category 21

Field GC

| Fused Polycyclic Hydrocarbons | MATE | | MW² | BP | COMP | Air | | SGC | GC Ramp | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Naphthalene | 5.0E4 | 7.5E5 | 128 | 218 | $C_{10}H_8$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Monoalkyl naphthalenes | 2.3E5 | 3.4E6 | | $240^+$ | | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Phenyl naphthalenes | | | 204 | 340 | $C_{16}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Dimethyl naphthalenes | 2.3E5 | 3.4E6 | 156 | $260^+$ | $C_{12}H_{12}$ | | ● | | | | | | | | ● | | | ● | | | | | | | |
| Acenaphthene; acenaphthylene | | | 154;152 | $270^{2}$ | $C_{12}H_{10}$; $C_{12}H_8$ | | ● | | | | | | | | ● | | | | ● | | | | | | |
| Anthracene | 5.6E4 | 8.4E5 | 178 | 340 | $C_{14}H_{10}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| 2,7-dimethylanthracene | | | 206 | 370 | $C_{16}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Phenanthrene | 1.6E3 | 2.4E4 | 178 | 340 | $C_{14}H_{10}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Methylphenanthrenes | 3.0E4 | 4.6E5 | 192 | $350^{t}$ | $C_{15}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Naphthacene | | | 228 | — | $C_{18}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| 1,2-benzanthracene | 4.5E1 | 6.7E2 | 228 | 435 | $C_{18}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| 9,10-dimethyl-1,2-benzanthracene | 2.6E-1 | 3.9E0 | 256 | — | $C_{20}H_{16}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Benzo(c)phenanthrene | 2.7E4 | 4.1E5 | 228 | — | $C_{18}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Chrysene | 2.2E3 | 3.3E4 | 228 | 448 | $C_{18}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Methylchrysenes | 1.8E3 | 2.7E4 | 242 | — | $C_{19}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Triphenylene | | | 228 | 438 | $C_{18}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Pyrene | 2.3E5 | 3.5E6 | 202 | 393 | $C_{16}H_{10}$ | | ● | | | | | | | | ● | | | | ● | | | | | | |
| 1-methyl pyrene | | | 216 | 410 | $C_{17}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| 1,2-benzonaphthacene | | | 278 | ~500 | $C_{22}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Benzo(b)chrysene | 1.6E4 | 2.4E5 | 278 | ~500 | $C_{22}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| 1,2:3,4-dibenzanthracene | 9.9E3 | 1.5E5 | 278 | — | $C_{22}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| 1,2:5,6-dibenzanthracene | 9.3E-2 | 1.4E0 | 278 | — | $C_{22}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Benzo[a]pyrene | 2.0E-2 | 3.0E-1 | 256 | 496 | $C_{20}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Benzo[e]pyrene | 3.0E3 | 4.6E4 | 256 | 493 | $C_{20}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Perylene | | | 256 | — | $C_{20}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Picene (dibenzo(a,i)phenanthrene) | 2.5E3 | 3.8E4 | 278 | 520 | $C_{22}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Dibenzo[a,h]pyrene | 3.7E3 | 5.6E4 | 302 | — | $C_{24}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Dibenzo[a,i]pyrene | 4.3E1 | 6.5E2 | 302 | — | $C_{24}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Dibenzo[a,ℓ]pyrene | 1.1E3 | 1.6E4 | 302 | — | $C_{24}H_{14}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Benzo[g,h,i]perylene | | | 277 | 500 | $C_{22}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |
| Coronene | | | 300 | 525 | $C_{24}H_{12}$ | | ● | | | | | | | | | ● | | | ● | | | | | | |

1 Health effects basis ($\mu g/m^3$) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100–300°C 4 GRAV BP >300°C

2-27-78

Category 22

## Fused Non-Alternant Polycyclic Hydrocarbons

| | MATE | | MW² | BP | COMP | Air | | SGC | GC Range | | | | | | TCO³ | GRAV⁴ | LC Fraction | | | | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air¹ | Water | | °C | | Gas | SASS | | 1 | 2 | 3 | 4 | 5 | 6 | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Indene and derivatives | 4.5E4 | 6.8E5 | 116 | 182* | $C_9H_8$ | | ● | | | | | | | | ● | | ● | | | | | | | | |
| Dicyclopentadiene | 1.6E4 | 2.4E5 | 132 | 170 | $C_{10}H_{12}$ | | ● | | | | | | | | ● | | ● | | | | | | | | |
| Fluorene and derivatives | | | 166 | 298* | $C_{13}H_{10}$ | | ● | | | | | | | | ● | | ● | | | | | | | | |
| Cyclopentanonaphthalene | | | 182 | 299 | $C_{13}H_{10}O$ | | ● | | | | | | | | ● | | ● | | | | | | | | |
| 2,3-benzofluorene | | | 216 | 402 | $C_{17}H_{12}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| Fluoranthene; tetrahydrofluoranthene | 9.0E4 | 1.4E6 | 202;<br>206 | 382;<br>365 | $C_{16}H_{10}$;<br>$C_{16}H_{14}$ | | ●<br>● | | | | | | | | | ●<br>● | | ●<br>● | | | | | | | |
| 1,2-benzofluorene | | | 216 | 413 | $C_{17}H_{12}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| 4-H-cyclopenta(def)phenanthrene | | | 190 | 353 | $C_{15}H_{10}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| Benzo(k)fluoranthene | 1.6E3 | 2.5E4 | 252 | 480 | $C_{20}H_{12}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| Benzo(e)fluoranthene | 9.0E2 | 1.4E4 | 252 | — | $C_{20}H_{12}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| Benzo(j)fluoranthene | 6.5E3 | 9.8E4 | 252 | 480 | $C_{20}H_{12}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| 1,2:5,6-dibenzofluorene | 1.3E4 | 2.0E5 | 266 | — | $C_{21}H_{14}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| 3-methyl cholanthrene | 3.8E0 | 5.6E1 | 268 | ~300 | $C_{21}H_{16}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| Indeno (1,2,3,c,d)pyrene | 1.6E3 | 2.4E4 | 276 | solid | $C_{22}H_{12}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |
| Truxene (tribenzylene benzene) | | | 340 | 365 | $C_{27}H_{18}$ | | ● | | | | | | | | | ● | | ● | | | | | | | |

1 Health effects base ($\mu g/m^3$) 2 Monoisotopic: lightest isotope of each atom 3 TCO BP 100-300°C 4 GRAV BP >300°C

2-27-78

Category 23

| Heterocyclic Nitrogen Compounds | MATE |  | MW[2] | BP | COMP | Air |  | Field GC |  |  |  |  |  |  | TCO[3] | GRAV[4] | LC Fraction |  |  |  |  |  |  |  | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Air[1] | Water |  | °C |  | Gas | SASS | SGC | GC Range 1 | 2 | 3 | 4 | 5 | 6 |  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |  |
| A. Pyridine and Substituted |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Pyridines |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Pyridine | 1.5E4 | 2.3E5 | 79 | 116 | $C_5H_5N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  | ● |  |  |  |  |  |  |
| Monosubstituted alkyl pyridines |  |  |  | 150+ |  |  | ● |  |  |  |  |  |  |  | ● |  |  |  | ● |  |  |  |  |  |  |
| phenyl pyridines |  |  | 162 | 270+ | $C_{11}H_9N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  | ● |  |  |  |  |  |  |
| Chloropyridine | 4.8E3 | 7.2E4 | 113 | 150± | $C_5H_4NCl$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  | ● |  |  |  |  |  |  |
| Disubstituted, polysubstituted pyridines | 2.7E4 | 4.1E5 |  | 160± |  |  | ● |  |  |  |  |  |  |  | ● |  |  |  | ● |  |  |  |  |  |  |
| B. Fused 6-membered Ring Heterocycles |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Quinoline, isoquinoline | 1.6E4 | 2.4E5 | 129 | 240± | $C_9H_7N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Methylquinolines, methylisoquinolines | 1.5E4 | 8.3E5 | 143 | 250± | $C_{10}H_9N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Dimethylquinolines, dimethylisoquinolines |  |  | 157 | 270± | $C_{11}H_{11}N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Acridine | 9.0E4 | 1.4E6 | 179 | 346 | $C_{13}H_9N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Dihydroacridine |  |  | 181 | 300 | $C_{13}H_{11}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Benzo(c)quinoline |  |  | 179 | 350 | $C_{13}H_9N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Benzo(f)quinoline |  |  | 181 | 350 | $C_{13}H_{11}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Benzo(h)quinoline |  |  | 179 | 338 | $C_{13}H_9N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Benz(a)acridine |  |  | 229 | 438 | $C_{17}H_{11}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Benz(c)acridine | 1.1E4 | 1.6E5 | 229 | 438 | $C_{17}H_{11}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Dibenz(a,j)acridine | 2.5E2 | 3.7E3 | 258 | — | $C_{21}H_{13}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Dibenz(a,h)acridine | 2.2E2 | 3.4E3 | 258 | — | $C_{21}H_{13}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Dibenz(c,h)acridine | 2.3E4 | 3.5E5 | 258 | — | $C_{21}H_{13}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Indeno(1,2-b)quinoline |  |  | 217 | 410 | $C_{16}H_{11}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| Indeno(1,2,3,i,j)isoquinoline |  |  | 203 |  | $C_{15}H_9N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| C. Pyrrole and Fused Ring Derivatives of Pyrrole |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Pyrrole | 2.7E3 | 4.0E4 | 67 | 130 | $C_4H_5N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Indole | 1.1E4 | 1.7E5 | 117 | 254 | $C_8H_7N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Methylindoles | 4.5E4 | 6.8E5 | 131 | 270± | $C_9H_9N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Carbazole | 2.3E4 | 3.4E5 | 167 | 355 | $C_{12}H_9N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  | ● | ● |  |  |  |
| Methylcarbazoles |  |  | 181 | 195 | $C_{13}H_{11}N$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● | ● |  |  |  |
| Benzo(a)carbozole | 1.9E4 | 2.8E5 | 217 | 450 | $C_{16}H_{11}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  | ● | ● |  |  |  |
| Dibenzo(a,g)carbozole | 6.0E3 | 9.0E4 | 267 | — | $C_{20}H_{13}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  | ● | ● |  |  |  |
| Dibenzo(a,i)carbozole | 1.2E4 | 1.8E5 | 267 | — | $C_{20}H_{13}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  | ● | ● |  |  |  |
| Dibenzo(c,g)carbozole | 1.0E3 | 1.5E3 | 267 | — | $C_{20}H_{13}N$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| D. Nitrogen Heterocycles containing additional Heteroatoms |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Benzothiazole | 4.3E3 | 6.4E4 | 135 | 231 | $C_7H_5NS$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |
| Methyl benzothiazoles | 4.7E3 | 7.1E4 | 149 | 238 | $C_8H_7NS$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  |

[1] Health effects basis (µg/m³) [2] Monoisotopic, lightest isotope of each atom [3] TCO BP 100-300°C [4] GRAV BP > 300°C

8-22-78

Category 24

**Heterocyclic Oxygen Compounds**

|  | MATE Air[1] | MATE Water | MW[2] | BP °C | COMP | Air Gas | Air SASS | SGC | GC Range 1 | GC Range 2 | GC Range 3 | GC Range 4 | GC Range 5 | GC Range 6 | TCO[3] | GRAV[4] | LC Fraction 1 | LC Fraction 2 | LC Fraction 3 | LC Fraction 4 | LC Fraction 5 | LC Fraction 6 | LC Fraction 7 | LC Fraction 8 | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Furan |  |  | 68 | 31 | $C_4H_4O$ | ● |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |
| Benzofurans |  |  | 118 | 174 | $C_8H_6O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |  |
| Dibenzofuran |  |  | 168 | 287 | $C_{12}H_8O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |  |
| Methyldibenzofurans |  |  | 182 | 300± | $C_{13}H_{10}O$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |
| Naphthofurans |  |  | 168 | 282 | $C_{12}H_8O$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |  |
| Benzo[b]naptho[2.3-d]furan |  |  | 218 | 395 | $C_{16}H_{10}O$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |
| Phenanthro[9.10-b]furan |  |  | 218 |  | $C_{16}H_{10}O$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |
| 1,9-benzoxanthene |  |  | 218 | 400 | $C_{16}H_{10}O$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |

[1] Health effects basis (ug/m³) [2] Monoisotopic, lightest isotope of each atom [3] TCO BP 100-300°C [4] GRAV BP > 300°C

2-27-78

Category 25

| Heterocyclic Sulfur Compounds | MATE |  | MW² | BP | COMP | Air |  | Field GC |  |  |  |  |  |  | TCO³ | GRAV⁴ | LC Fraction |  |  |  |  |  |  |  | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Air¹ | Water |  | °C |  | Gas | SASS | SGC | GC Range 1 | 2 | 3 | 4 | 5 | 6 |  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |  |
| Thiophene | 4.5E3 | 6.8E4 | 84 | 34 | $C_4H_4S$ | ● |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |
| Methylthiophenes | 2.3E4 | 3.4E5 | 98 | 112 + | $C_5H_6S$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |  |
| Dimethylthiophenes |  |  | 112 | 140 ± | $C_6H_8S$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |  |
| Trimethyl; and tetramethyl |  |  | 126 | 170 ±; | $C_7H_{10}S$; |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |  |
| thiophenes |  |  | 140 | 170 ± | $C_8H_{12}S$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |  |
| 2,2'-Bithiophene |  |  | 166 | 260 | $C_8H_6S_2$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |  |
| Benzo[b] thiophene | 2.3E4 | 3.5E5 | 134 | 221 | $C_8H_6S$ |  | ● |  |  |  |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |  |
| Dibenzothiophene |  |  | 184 | 332 | $C_{12}H_8S$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  | ● |  |  |  |  |  |
| Benzonaphthathiphene | 9.9E2 | 1.5E4 | 234 | 430 | $C_{16}H_{10}S$ |  | ● |  |  |  |  |  |  |  |  | ● |  |  |  | ● |  |  |  |  |  |

1 Health effects basis (ug/m³) 2 Monoisotopic, lightest isotope of each atom   3 TCO BP 100 300°C   4 GRAV BP > 300°C

2-27-78

Category: 26

**Organometallics**

|  | MATE |  | MW² | BP | COMP | Air |  | Field GC SGC | GC Range |  |  |  |  |  | TCO³ | GRAV⁴ | LC Fraction |  |  |  |  |  |  |  | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Air¹ | Water |  | °C |  | Gas | SASS |  | 1 | 2 | 3 | 4 | 5 | 6 |  |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |  |
| **A. Alkyl or Aryl Organometallics** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Trimethyl arsine |  |  | 120 | 52 | $As(CH_3)_3$ | ● |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |
| Alkyl lead (TEL) | 1.0E2 | 1.5E3 | 323 | 200 | $Pb(C_2H_5)_4$ |  | ● |  |  |  |  |  |  |  | ● |  | ● |  |  |  |  |  |  |  |  |
| Alkyl mercury (DMM) | 1.0E1 | 1.5E2 | 226 | 96 | $Hg(CH_3)_2$ | ● |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |
| Organotin | 1.0E2 | 1.5E3 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Organogermanes | 3.2E4 | 4.7E5 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **B. Sandwich Type Organometallics** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Ferrocene | 6.0E4 | 9.0E5 | 186 | - | $Fe(C_5H_5)_2$ |  | ● |  |  |  |  |  |  |  |  | ● | ● |  |  |  |  |  |  |  |  |
| Nickelocene | 3.5E3 | 5.2E4 | 189 | - | $Ni(C_5H_5)_2$ |  | ● |  |  |  |  |  |  |  |  | ● | ● |  |  |  |  |  |  |  |  |
| Dibenzene chromium |  |  | 206 | - | $Cr(C_6H_6)_2$ |  | ● |  |  |  |  |  |  |  |  | ● | ● |  |  |  |  |  |  |  |  |
| **C. Metal Porphyrins and Other Chelates** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Complexed Vanadium |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Nickel |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Copper | 3.0E3 | 4.5E4 |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Iron |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Tin |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Zinc |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

1 Health effects basis (μg/m³) 2 Monoisotopic, lightest isotope of each atom 3 TCO BP 100 300°C 4 GRAV BP > 300°C

2-27-78

## Appendix B

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